

SYNTHESIS OF COMPOSITE
NANOPARTICLES WITH DIFFERENT CORE
NANOPARTICLES COATED WITH A
MAGNETIC FERRITE SHELL

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SINTEZA KOMPOZITNIH NANODELCEV Z
NANOSOM MAGNETNIH FERITNIH PLASTI NA
RAZLIČNE JEDRNE NANODELCE
Doktorska disertacija

Supervisor: Prof. Dr. Darko Makovec

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To my mother and grandmother

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Abstract

Composite nanoparticles represent novel materials where coupling between properties of different materials inside a single nanoparticle could lead to improved or even entirely new properties. One of the possible approaches for synthesis of the composite nanoparticles is deposition of a shell made of one material onto the surfaces of core nanoparticles made of another material. A magnetic shell of spinel ferrite can be deposited onto the core nanoparticles using a simple controlled co-precipitation method. The method is based on heterogeneous nucleation of a product of co-precipitation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions on the surfaces of the core nanoparticles in the aqueous suspension. The supersaturation of the precipitating product is closely controlled by a controlled release of the Fe^{3+} ions with thermal decomposition of a coordination compound $[\text{Fe}((\text{H}_2\text{N})_2\text{C}=\text{O})_6(\text{NO}_3)_3]$ (Fe-urea complex). This method was already successfully used for the deposition of soft-magnetic maghemite layers on the surfaces of hard-magnetic hexaferrite core nanoplatelets. In my thesis the method was modified to allow close control over the thickness of the deposited maghemite layers on the cores. The thickness of the maghemite layers was controlled by varying the ratio between the iron precursors and the hexaferrite cores or by deposition of the layers in two subsequent steps. Morpho-structural characterization using a combination of X-ray diffractometry (XRD), Raman spectroscopy, atomic-resolution transmission (HREM) and scanning-transmission (HAADF STEM) microscopy revealed that the bi-magnetic composite nanoplatelets displayed an incredibly uniform maghemite-hexaferrite-maghemite sandwich-type structure. The layers of the uniform thickness grew epitaxially exclusively at the basal surfaces of the hexaferrite nanoplatelets. Varying the layer thickness enabled tuning magnetic properties of the bi-magnetic nanoplatelets. Magnetic measurements (VSM) showed that the bi-magnetic nanoplatelets displayed a single-phase hysteresis loop indicating that the two magnetically different phases are rigidly exchange coupled. The nanoplatelets retained desired out-of-plane magnetization of the hexaferrite cores while saturation magnetization M_s was significantly improved with the maghemite deposition. The M_s increased proportionally with the increasing layer thickness. However, the increase in M_s was accompanied by a decrease of coercivity H_C , which was related to exchange coupling between the two magnetically different phases and to structural strains induced in the hexaferrite core by the epitaxial layers.

In the second part of my thesis I tried to implement the controlled co-precipitation method for coating the spinel-ferrite shell onto the surfaces of ferroelectric bismuth titanate (BIT) core nanoplatelets. Combining the magnetic shell with the ferroelectric core would be beneficial for controlling the nanoplatelets in the suspension with an applied magnetic field or the composite nanoparticles could be used as building blocks for magnetoelectric composites. However, it was found that the method could not be directly transferred for deposition of the magnetic layers onto the surfaces of the BIT cores. Fe-rich nanoparticles deposited onto the surfaces of the cores remained amorphous. Moreover, the nanoparticles remain amorphous even after hydrothermal treatment or after annealing above 500 °C, whereas at 700 °C the iron-rich phase react with BIT core

nanoplatelets. The reason for the observed differences between the deposition of the spinel-ferrite shell onto the different core nanoparticles was ascribed to partial dissolution of the BIT cores in the presence of urea released during decomposition of the Fe-urea complex.

Povzetek

Kompozitni nanodelci predstavljajo nove materiale, ki spajajo v posameznem nanodelcu najmanj dva različna materiala. Sklopitev lastnosti različnih materialov v kompozitnem nanodelcu lahko pripelje do izboljšanih ali celo povsem novih lastnosti.

Kompozitne nanodelce lahko sintetiziramo z nanosom tanke plasti enega materiala na površino nanodelcev drugega materiala. Tanko plast magnetnega spinelnega ferita lahko nanesemo na površino jedrnih nanodelcev s kontroliranim soobarjanjem. Metoda temelji na soobarjanju $\text{Fe}^{3+}/\text{Fe}^{2+}$ ionov ter heterogeni nukleaciji produkta na površini jedrnih nanodelcev v vodni suspenziji. Nizko stopnjo prenasičenja, ki je potrebna za izključno heterogeno nukleacijo produkta na površini jedrnih nanodelcev, dosežemo z vezavo Fe^{3+} ionov v koordinacijsko spojino $[\text{Fe}((\text{H}_2\text{N})_2\text{C}=\text{O})_6(\text{NO}_3)_3]$. Termična razgradnja spojine omogoča kontrolirano sproščanje Fe^{3+} ionov homogeno po celotnem reakcijskem volumnu. S tem postopkom lahko nanesemo tanko plast mehkomagnetnega železovega oksida maghemita na površino trdomagnetnih heksaferitnih jedrnih nanoploščic. V svojem delu sem metodo prilagodil tako, da lahko z njo natančno kontroliramo debelino maghemitne plasti. Debelino plasti lahko uravnavamo s spreminjanjem razmerja med reaktanti in heksaferitnimi nanoploščicami ali z nanosom plasti v dveh zaporednih stopnjah. Morfološko-strukturno karakterizacijo kompozitnih nanoploščic smo izvedli z rentgensko praškovno difraktometrijo (XRD), Ramansko spektroskopijo ter s presevno (HREM) in vrstično-presevno (STEM HAADF) elektronsko mikroskopijo. Karakterizacija je pokazala, da izkazujejo sintetizirane kompozitne nanoploščice izjemno enakomerno strukturo. Maghemitna plast enakomerne debeline raste epitaksialno izključno na obeh bazalnih površinah heksaferitnih nanoploščic. Magnetne meritve (VSM) so pokazale, da izkazujejo kompozitne nanoploščice gladko histerezo zanko, kot jo izkazujejo enofazni delci. Gladka histerezo zanka potrjuje, da sta različna magnetna materiala v kompozitni nanoploščici magnetno sklopljena. Kompozitne nanoploščice izkazujejo enosno magnetno anizotropijo v smeri pravokotno na nanoploščico. Z debelino nanešene maghemitne plasti se nanoploščicam povečuje nasičena magnetizacija M_s , medtem ko se jim neproporcionalno močno zniža koercitivnost H_C . Vzrok za znižanje H_C lahko pripišemo sklopitvi lastnosti med mehkomagnetno in trdomagnetno fazo ter napetostim v strukturi heksaferitnih jeder, ki so posledica nanosa epitaksialnih maghemitnih plasti.

V drugem delu doktorske naloge sem želel uporabiti metodo kontroliranega soobarjanja za nanos maghemitnih plasti na površino jedrnih nanoploščic ferroelektričnega bizmutovega titanata (BIT). Nanos magnetne plasti na nanoploščice BIT bi lahko omogočil urejanje feroelektričnih nanoploščic v suspenziji z zunanjim magnetnim poljem ali pa bi takšne kompozitne nanodelce lahko uporabili kot gradnike

pri pripravi magneto-električnih kompozitov. V delu sem ugotovil, da metode soobarjanja ni mogoče uporabiti za nanos maghemitne plasti na površino nanoploščic BIT. Produkt, prisoten na površini nanoploščic BIT po nanosu, je ostal amorfen. Nanodelci niso kristalizirali niti po naknadni hidrotermalni obdelavi produkta niti po segrevanju na temperaturi višji od 500 °C, medtem ko pri 700 °C obe fazi zreagirata. Razlog za razliko v nanosu feritne plasti na površino različnih jedrnih nanoploščic lahko pripišemo delnemu raztapljanju BIT v reakcijski mešanici. Ioni, sproščeni pri raztapljanju, motijo kemijske reakcije nastanka feritne plasti.

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Abbreviations

AFM	... Antiferromagnetic
BIT	... Bismuth titanate
BSHF	... Barium hexaferrite doped with scandium
CNP	... Bi-magnetic composite nanoplatelets
CS	... Core/shell
DLVO	... Derjaguin-Landau-Verway-Overbeek theory
FM	... Ferro/ferrimagnetic
HAADF	... High angle annular dark field
HEN	... Heterogeneous nucleation
HON	... Homogeneous nucleation
HF	... Hexaferrite
HRTEM	... High resolution transmission electron microscopy
M	... Maghemite
ME	... Magnetoelectric
MNP	... Magnetic nanoparticles
MPI	... Magnetic particle imaging
MRI	... Magnetic resonance imaging
JSI	... Jožef Stefan Institute
IPS	... International Postgraduate School
PZC	... Point of zero charge
PZT	... $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$
RKKY	... Runderman-Kittel-Kasuya-Yosida theory
STEM	... Scanning transmission electron microscopy
SAED	... Selected area electron diffraction
TEM	... Transmission electron microscopy
TEOS	... Tetraethylorthosilicate
VDW	... Van der Waals
VSM	... Vibrating sample magnetometer
XRD	... X-ray diffraction

Symbols

A	... Surface area
A_H	... Hamaker constant
A_h	... Exchange constant
a	... Particles radius
B	... Magnetic induction
$ BH _{MAX}$	... Energy product
c_L	... Precursor concentration in suspension
c_{min}	... Minimum concentration
c_S	... Solubility of solid phase
d_s	... Thickness of soft-magnetic layer
d_{cs}	... Critical thickness of the soft-magnetic layer
d_{33}	Piezoelectric constant
δ_h	... Thickness of the hard-magnetic domain wall
ϵ	Relative dielectric constant
E_{ex}	... Exchange energy
E_e	... Electrostatic energy
E_{dd}	... Energy of dipole-dipole interactions
E_m	... Magnetic energy
E_{ster}	... Steric energy
E_{struct}	... Structural energy
E_{total}	... Total interparticle energy
E_{VDW}	... Van der Waals energy
ΔE	... Energy barrier
f	... Parameter describing the influence of the foreign particles in the nucleation barrier
ΔG	... Gibbs free enthalpy
ΔG_N	... Nucleation activation energy
γ	... Interfacial energy
γ_{ef}	... Specific interfacial free energy
H	... Magnetization
h	... Distance between the particle's surfaces
H_C	... Coercive field
J	... Exchange integral
J_n	... Nucleation rate
K_i	... Anisotropy constant
k_B	... Boltzmann constant
κ	... Ratio between the anisotropy constant and energy product
l	... Distance between the particles
M	... Magnetic moment
M_R	... Saturation magnetization

M_S	... Remanent magnetization
ΔM_{rev}	... Reversible magnetization
m	... Magnetic moment
μ_0	... Permeability of free space
μ	... Magnetic permeability
μ_L	... Chemical potential of entity in the solution
μ_S	... Chemical potential of entity in the solid
n	... Number of precursors
P	... Pressure
S	... Supersaturation
ρ	... Ionic density
T	... Temperature
T_B	... Blocking temperature
T_C	... Curie temperature
T_N	... Neel temperature
t_1	... Incubation time
τ	... Relaxation energy
V	... Volume
V_{total}	... Total volume
v_h	... Volume fraction of hard-magnetic phase
χ	... Magnetic susceptibility
σ	... Molecular diameter
ϕ	... Angle between two vectors
ψ_0	... Surface potential
ψ_D	... Stern potential
ζ	... Zeta potential

Chapter 1

Introduction

1.1 Magnetic Properties of Materials

Applications of magnetic materials base on their response to an external magnetic field. The response of the material to the magnetic field strongly depends on a type of atoms it contains and their arrangement in its crystal structure. Magnetism of atoms originates from the movement of electrons around the nucleus (orbital movement) and around its own axis (spin movement). Each electron has a magnetic moment. The magnetic moment of the atom is the vector sum of all magnetic moments of the electrons associated with it. Two possible situations can arise:

1. In atoms with paired valent electrons the magnetic moments of the electrons are oriented in the way that they cancel each other out. Such atoms have no net magnetic moment and this condition leads to diamagnetism.
2. In atoms with unpaired valent electrons the magnetic moments of the electrons are only partially cancelled. Such atoms possess a net magnetic moment and they are referred to as magnetic atoms.

The macroscopic behaviour of the magnetic moments can be described with a few parameters. The response of the material to an external magnetic field is relevant to magnetic energy, E_m :

$$E_m = -\mu_0 \cdot m \cdot H \quad (1.1)$$

where μ_0 is the permeability of free space, m is the magnetic moment and H is the magnetic field strength. The density or flux of the magnetic lines of the material describes magnetic induction B and can be expressed with the magnetic energy (Equation 1.2). The relationship between magnetic induction, B , and magnetic field H (Equation 1.3) can be expressed from Equation 1.1 and 1.2. However, Equation 1.3 can be only applied for the systems in free space. General relationship between B and H is described with Equation 1.4, where M is material magnetization defined as the magnetic moment per unit volume or mass of the material (Equation 1.5) [1].

$$E_m = -mB \quad (1.2)$$

$$B = \mu_0 \cdot H, \text{ in free space, where } M = 0 \quad (1.3)$$

$$B = \mu_0 \cdot (H + M) \quad (1.4)$$

$$M = m/V \quad (1.5)$$

The magnetic properties of a material are not characterized only by the magnitude of the magnetization but also by the way how the magnetization depends on the applied magnetic field (M/H curves). The ratio between M and H ascribes magnetic susceptibility χ (Equation 1.6).

$$\chi = dM/dH \quad (1.6)$$

Traditionally, materials are classified according to the dependency of their magnetization M on the magnetic field strength H .

When the material is placed in a magnetic field, the individual atomic moments in the material contribute to its overall response. The material is classified as diamagnetic when it consists of atoms with paired valent electrons. Their M linearly changes with H , however the susceptibility χ is small ($\chi < -10^{-6}$) and negative. Oppositely, materials consisting of atoms with unpaired electrons are classified as paramagnets. In the absence of the magnetic field, magnetic moments of individual atoms are randomly orientated. When the paramagnetic material is placed in a magnetic field, magnetic moments tend to align parallel to the direction of the applied field. The M increases linearly with the H [1, 2].

In ferromagnetic materials, just as in the paramagnetic ones, magnetic moments are present. The difference between the two is that in the ferromagnetic materials, the magnetic moments of neighbouring ions are aligned parallel. The parallel alignment of the magnetic moments leads to the strong response (i.e., high susceptibility), when the material is exposed to the field. However, this does not mean that the whole specimen is uniformly magnetized. For bulk magnetic material it is energetically more favourable to be divided into small regions called domains. Within each domain, the magnetic moments are aligned parallel; however, the orientation of magnetic moments varies from one domain to another. The orientation of magnetic moments is determined by the direction of the spin and orbit movements. The interaction that occurs between the magnetic moments is called the exchange interaction. The exchange interactions between magnetic moments in the atom can be described in terms of the exchange energy:

$$E_{ex} = -2 \cdot J \cdot S_1 \cdot S_2 \cdot \cos\Phi \quad (1.7)$$

where Φ is the angle between spin vectors S_1 and S_2 and J is the exchange integral. For $J > 0$, E_{ex} will be lower for parallel magnetic moment arrangement and highest for anti-parallel ordering [3].

While ferromagnetic materials have only one magnetic lattice where magnetic moments are aligned parallel, the antiferromagnetic and ferrimagnetic material can be considered as a superposition of two oppositely directed magnetic sublattices. In ferrimagnetic materials, the magnetic moments are divided into two different sublattices, whereas their alignment is parallel within one sublattice. The magnetic moment of one sublattice prevails over the other, resulting in a net magnetic moment. In ferrimagnetic materials, the magnetic cations are separated by anions. Thus instead of direct exchange-coupling between the metal ions, as in the ferromagnetic materials, the metal ions are coupled through the oxygen ions. This type of interaction is called super-exchange.

Ferro and ferrimagnetic materials display spontaneous magnetization at room temperature. However, when the materials are heated above a certain temperature they become paramagnetic. The point where transition from ferro/ferri magnetic to paramagnetic state occurs is called the Curie temperature T_C . As the temperature increases, thermal motion competes with the ferromagnetic tendency for aligning the magnetic moments. When the temperature rises above T_C , the transition occurs and the system no longer displays a spontaneous magnetization. At T_C the permeability of the material drops suddenly and both coercivity and remanence become zero [4].

One of the main characteristics of magnetic materials is the magnetization curve – hysteresis loop. Hysteresis is the result of the irreversible magnetization process which means that after the removal of an applied magnetic field, partial relaxation of the magnetic moments in the material occurs. In bulk, the partial relaxation of the magnetic moment can be explained with the domain structure of the material. Figure 1.1 a) shows hysteresis loop of the multi-domain magnetic material. Domain structure is presented in the small boxes where arrows represent the direction of the magnetic moments in a single domain. In a demagnetized state (A), the directions of magnetic moments in the individual domains are distributed randomly. By applying the small external magnetic field, the domain walls can be moved across the material. At first the magnetic moments remain orientated in a direction of easy axis, but domains close to the field direction grow at the expense of those magnetized away from field directions (wall displacement) (B). With further increasing the magnetic field, magnetic moments rotate toward the field direction until the saturation magnetization, M_s , is reached (C). At a fully saturated stage the domain structure disappears due to the parallel alignment of the magnetic moments. When the magnetic field is decreased towards zero, the irreversibility of the domain motion occurs resulting in the partial relaxation of the magnetic moments (D). The magnetization at the field 0 is called remanent magnetization or remanence M_R . With applying the magnetic field in reverse direction $-H$, the magnetization of the material can be reduced to 0 (E). Field required for the complete demagnetization of the material is referred to as coercive field or coercivity H_C . With further decreasing of the magnetic field in the reverse direction, the whole magnetization process repeats to the point where the saturation value is reached again (F) [1, 5].

Ferro- and ferrimagnetic materials can be classified according to the shape of the hysteresis loop into magnetically hard and soft materials (Figure 1.1 b). The materials are classified as soft-magnetic when relatively low external magnetic field is required for their saturation. Soft magnetic materials have very narrow M/H loops – high M_s and relatively low H_C . Contrary, hard-magnetic materials require a high magnetic field for their saturation. They have broad, square M/H loops – relatively low M_s and high H_C . They are suitable for permanent magnets because when the magnetic field is removed, they remain in a magnetized state [1, 4].

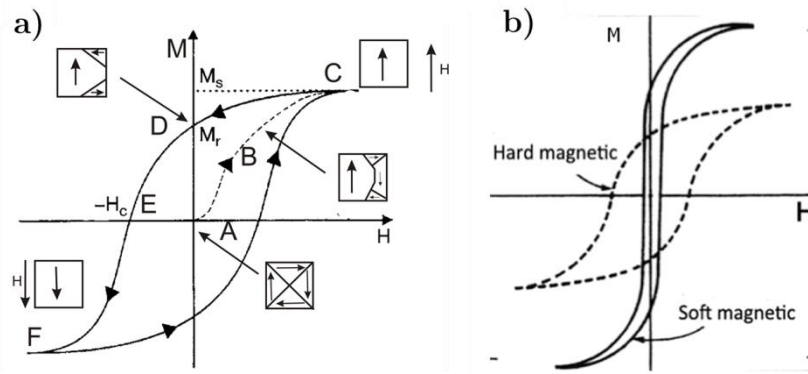


Figure 1.1: Hysteresis loop a) with the domain distribution [3] and b) of hard and soft magnetic materials [4].

1.1.1 Magnetic properties of nanoparticles

Magnetism of nanoparticles is an area of intense development that touches many fields including material science, biology, physics, medicine, etc. Understanding the magnetic properties of nanomaterials is a central issue in the field of magnetic materials. Nowadays magnetic nanoparticles are used as the active component of ferrofluids, recording media, high-frequency electronics, biomedicine, etc. [6].

When we deal with particles, their physical properties are size dependent. From the viewpoint of magnetism, single-domain particles, i.e., particles with size comparable (or smaller) to the sizes of magnetic domains in the corresponding bulk materials are the most interesting. In the case of bulk defect-free materials, their intrinsic magnetic properties (M_s , H_c , T_c) depend on the chemical and crystallographic structure and the size and shape of the material is not crucially important. However, when dealing with materials at the nano-size range, their magnetic properties are strongly influenced by the so-called finite-size and surface effects.

Figure 1.2 shows the coercivity in dependence of the particle size. Magnetic bulk materials are divided into magnetic domains which are separated with domain walls. As the particle size decreases towards some critical particle diameter, the formation of domain walls becomes energetically unfavourable. With decreasing the particle size the H_c of ferromagnetic particles increases to the maximum value when the particles are in single domain [1]. When the particle size is equal or smaller to critical value where particles become single-domain D_s , the magnetization reversal no longer proceeds with the domain wall motion. Magnetization reversal that instead proceeds with simultaneous rotation of all the spins in the particles (or by physical rotation of the particle) requires a larger external field. With further decreasing the particle size, the energy barrier required for spin rotation decreases due to the thermal effect. Consequently, the magnetic field required to obtain zero magnetization decreases. The coercivity is zero when the particle size is below critical value D_p . At this stage the nanoparticles come to the superparamagnetic state (see below) [7-9]. For example, magnetic spinel iron oxides become superparamagnetic at the size below approximately 20 nm, while barium hexaferrite exhibits superparamagnetic behaviour below 10 nm [3].

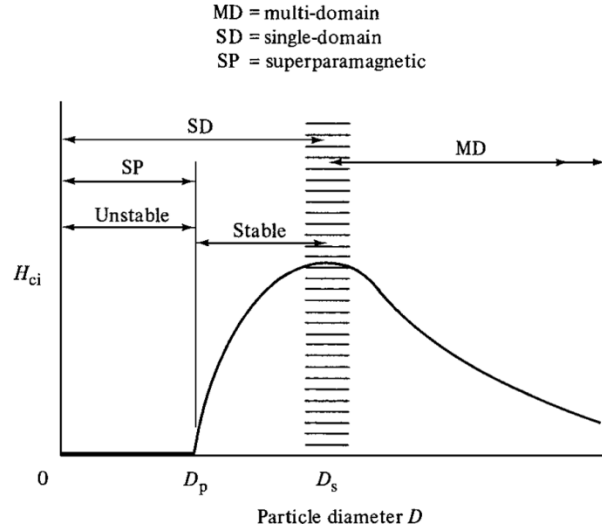


Figure 1.2: The coercivity in dependence of the particle size [1].

Decreasing the particle size leads also to some surface effects. With decreasing the particle size, the proportion of the surface atoms compared to those in the interior of the particle increases. Therefore, nanoparticles can be presented as the “core/shell” structures. The “core” usually displays similar magnetic behaviour as the bulk material, while a much higher magnetic disorder is present at the surface. Due to competition between the “core” and “shell” magnetic orders some effects can occur [10]. One of the examples of the surface effects in the magnetic properties of the materials is the reduction of magnetization in ferrite nanoparticles. For example, in bulk spinel ferrites, the division of the 24 cationic sites in the unit cell into two magnetic sublattices is the result of a balance between competing antiferromagnetic interactions. When some exchange bonds are removed at the surface, there can be frustration and spin disorder which leads to the reduced magnetization in nanoparticles compared to the bulk counterparts [6].

1.1.1.1 Superparamagnetism

An important phenomenon that occurs in magnetic nanoparticles and is related to the decreasing of the particle size is superparamagnetism. Superparamagnetism can be explained with behaviour of a well-isolated single magnetic nanoparticle. Consider an assembly of uniaxial, single-domain particles, with anisotropy energy;

$$E(\theta) = K_i \cdot V \cdot \sin^2 \theta \quad (1.8)$$

where K_i is the anisotropy constant and θ is the angle between the magnetization, M , and the easy axis. If the volume of each particle is V , then the energy barrier ΔE that must be overcome for reversing the particle magnetization is $K_i V$. With decreasing the particle size, the thermal energy, $k_B T$, exceeds the energy barrier $K_i V$ and the thermal fluctuations induce random flipping of the magnetic moments. For $k_B T > K_i V$ the system behaves like a paramagnet, however, instead of atomic magnetic moments the giant – super moment occurs inside each particle. This system is referred to as superparamagnetic. The simplest model to represent the characteristic time of the thermal fluctuation of magnetic moments is given by the Neel-Brown expression

(Equation 1.9) where τ is the relaxation time of the moment of the particle; k_B is the Boltzmann's constant, and $\tau_0 \approx 10^{-9}$ s.

$$\tau = \tau_0 \cdot \exp(K_i \cdot \frac{V}{k_B} \cdot T) \quad (1.9)$$

If the time of observation is longer to the relaxation time τ nanoparticles will appear as superparamagnetic. The observation time varies for different characterization methods (e.g. 100s for SQUID magnetometry, 10^{-8} s for M to Mössbauer spectroscopy). As paramagnetic materials the superparamagnetic materials display a large increase in the magnetization when exposed to the magnetic field, while it drops to zero when the field is not present. However, the magnetization of superparamagnetic nanoparticles is several orders higher. The magnetization curve of the superparamagnetic materials (Figure 1.3) has a sigmoid shape and can be defined with the Langevin function [1, 2]:

$$M_S \cdot L(x), \quad L(x) = \coth(x) - \frac{1}{x}, \quad x = \frac{M_S \cdot V \cdot H}{k \cdot T} \quad (1.10)$$

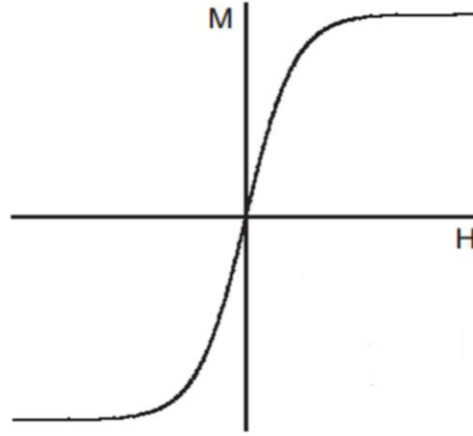


Figure 1.3: The M/H curve of superparamagnetic nanoparticles.

1.1.2 Magnetic properties of hard/soft bi-magnetic nanoparticles

Composite nanoparticles, which combine two different magnetic materials, are referred to as bi-magnetic nanoparticles. The bi-magnetic nanoparticles represent a novel class of nanostructured materials where we could precisely engineer magnetic properties of the individual nanoparticle to make them relevant for a specific application [11-14].

An exchange bias resulting from the coupling between the ferromagnetic and antiferromagnetic material represents an extra source of anisotropy, which increases the superparamagnetic limit – an important property in miniaturization of recording media [15, 16]. An even more important property, exchange coupling between the soft-magnetic and hard-magnetic materials combined at the nanolevel can result in an increased energy product $|BH|_{MAX}$, a figure of merit for the quality of the magnets. These bi-magnetic nanoparticles could be used as building blocks for the exchange spring permanent magnets with improved magnetic properties or the exchange coupling effect could be used to tune the properties of the nanoparticles. However, between the magnetic materials combined in a composite, different exchange interactions could occur. The exchange

coupling interaction between magnetically different materials will be described in the next section. Since in my thesis I studied the synthesis of the hard/soft composite nanoparticles, the direct exchange coupling between those two magnetic materials will be described in detail.

1.1.2.1 Exchange coupling interactions in bi-magnetic nanoparticles

The dipole-dipole interactions are presented in almost every spin system, but for instance in concentrated magnetic systems (e.g. thin films, composites) other interactions such as exchange interactions can prevail over them. The exchange interactions describe interactions between electron spins in one material or interactions between the spins of different materials at their interface. They have been mostly studied on the thin film heterostructures composed of alternating magnetic or magnetic/non-magnetic layers. When the magnetic layers are in direct contact, the direct exchange coupling between them occurs. When the magnetic layers are separated by the nonmagnetic layer, the spin polarization mediated through non-magnetic layer resulted in indirect exchange coupling. [2, 12, 17].

1.1.2.1.1 Indirect exchange coupling

The indirect exchange coupling appears between ferromagnetic layers separated by non-magnetic metal spacer layer. It was firstly observed in Fe/Cr/Fe and Co/Ru/Co systems. The sign and magnitude of the exchange coupling that occurs in such systems oscillates as a function of the non-magnetic spacer thickness. The purpose of preparing such a composite is to create the artificial magnets used for magneto-electronic devices. By tuning the spacer thickness, the interlayer coupling can be chosen to be ferromagnetic, antiferromagnetic or zero. [2, 18].

Another type of indirect exchange coupling interaction is dipolar coupling. Compared to the previous case, indirect dipolar exchange coupling appears only between ferromagnetic layers that are not perfectly smooth. This is also known as the “orange-peeling” effect. The magnitude of the dipolar coupling depends on the thickness and roughness of the non-magnetic layer and it is few magnitudes smaller compared to the coupling between perfectly smooth ferromagnetic layers [2].

1.1.2.1.2 Direct exchange coupling

Direct exchange coupling occurs when two magnetically different materials are in close contact. More precisely, the exchange interactions occur between the spins of the materials at their interfaces. Due to the large importance of the direct exchange coupling in the applications such as permanent magnets, recording and storage media, the effect has been mainly investigated on the thin film systems. According to the magnetic properties of the interacting materials, direct exchange coupling can be divided into two classes: exchange bias occurring between the ferro/ferrimagnetic and antiferromagnetic phases [16] and exchange spring coupling resulting from coupling between hard-magnetic and soft-magnetic phases [19].

My work comprises the synthesis of the bi-magnetic composite nanoparticles combining soft-magnetic maghemite layers deposited onto the surface of the hard-magnetic barium hexaferrite cores. Due to this, only the properties of the bi-magnetic materials combining hard/soft phases will be overviewed in detail.

The direct magnetic coupling between the magnetically hard and soft materials could lead to an improved energy product $|BH|_{MAX}$. $|BH|_{MAX}$ is a measure of the maximum magnetostatic energy that could be stored in a magnetic material. It can be ascribed by

plotting the area below the hysteresis loop. Therefore for the maximum $|BH|_{MAX}$, the material with high M_s and H_C is required (perfect square shaped hysteresis loop) [20]. Generally, for the materials with sufficiently high H_C values ($H_C \geq 2\pi M_s$), the theoretical limit for the energy product is limited only by saturation M_s and is given as:

$$(BH_{MAX}) \leq \frac{J_s^2}{4\mu_0} \text{ where } J_s = \mu_0 M_s \quad (1.11)$$

Considering these limitations $|BH|_{max}$ can be reached only with materials that have a sufficiently high uniaxial magnetocrystalline anisotropy ($K_i \gg Js^2/4\mu_0$). Unfortunately, the hard-magnetic materials generally show moderate M_s . Alternative approach for the preparation of materials with improved H_C and M_s is to design composite nanoparticles consisting of soft magnetic and hard magnetic materials. Here the hard magnetic phase provides high H_C while the soft magnetic phase provides high M_s . If the two phases are rigidly directly exchange coupled at a nanolevel, the nanocomposite will magnetize uniformly, as a single-phase material. [13, 14, 19, 20].

The most important parameter for the hard/soft bi-magnetic composite nanoparticles is the dimension of the soft phase. It was found that for effective exchange coupling between both phases, the thickness of the soft-magnetic layer d_{cs} should not exceed twice the domain wall thickness of the hard-magnetic phase δ_h . Therefore the nanocomposite will magnetize uniformly if the thickness of the soft-magnetic layer is below the δ_h [19-21].

For the thin soft magnetic layer ($d_s < \delta_h$), the two magnetically different phases reverse at the same nucleation field, because they are rigidly exchange coupled. Rigid coupling between magnetically different phases results in a smooth, single-phase hysteresis loop. The system is characterized by averaged magnetic properties of the two phases.

In the case when the d_s exceeds d_{cs} , the coercivity of the soft layers drops quickly and reduces the hard-magnetic properties of the system. This arises due to the fact that switching of magnetization starts to occur at a lower nucleation field than in the hard magnetic one. The magnetic moments in the soft magnetic layer remain parallel to the hard magnetic ones for the fields less than the nucleation field (or the exchange field H_{ex}). With increasing the reversal magnetic field ($H > H_{ex}$), the magnetic reversal process proceeds via twisting of the magnetic moments in the soft-magnetic phase. This occurs because at the interface the magnetic moments in the soft phase are pinned by the hard-magnetic phase, but moments near the surface are free and follow the external magnetic field. With removing the external magnetic field, the magnetic moments in the soft phase align parallel with the magnetic moments in the hard phase and magnetic materials exhibit reversible demagnetization [21]. Because of this specific magnetic behaviour which resembles the elastic motion of a mechanical spring, such magnets where d_s exceed d_{cs} have been referred to as exchange-spring magnets. However, such reversal mechanism occurs for the systems with thick soft-magnetic layer ($d_s > d_{cs}$). On contrary, in the case of thin soft-magnetic layer ($d_s < d_{cs}$), the two magnetically different phases reverse simultaneously as they are rigidly coupled.

The exchange coupling between the hard-magnetic and soft-magnetic phase results in a smooth hysteresis loop similar to the one of the single-phase magnetic materials (as is shown in Figure 1.4 a). On the contrary, if the magnetically different phases were not exchange coupled, the material would exhibit a constricted loop (as it is shown in Figure 1.4 b). The constricted loop is also displayed by composites where $d_s > d_{cs}$ [19].

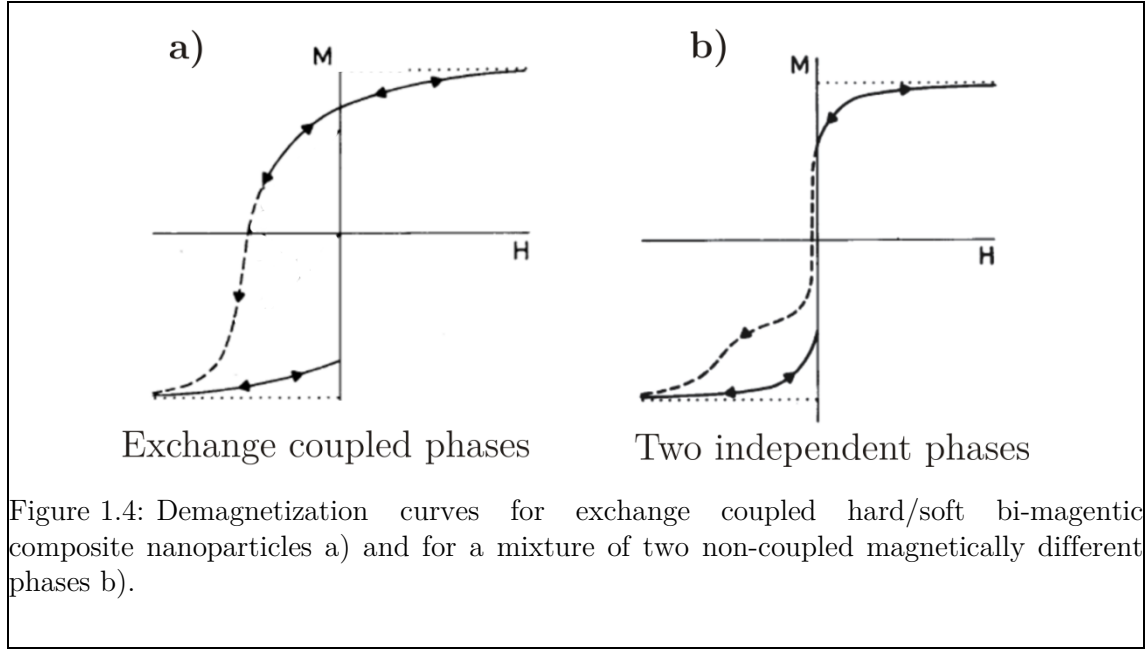


Figure 1.4: Demagnetization curves for exchange coupled hard/soft bi-magnetic composite nanoparticles a) and for a mixture of two non-coupled magnetically different phases b).

1.2 Structure and Magnetic Properties of Ferrites

1.2.1 Cubic ferrites

Cubic or spinel ferrites have general formula MeFe_2O_4 , where Me represents a divalent metal cation: Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Mg^{2+} , or Cd^{2+} . They are referred to as spinel ferrites since their structure is closely related to the mineral spinel (MgAl_2O_4). In spinel ferrites, oxygen atoms form a face-centred cubic crystal structure (fcc) in which two kinds of interstitial sites occur: tetrahedral A sites (surrounded by 4 oxygen ions) and octahedral B sites (surrounded by 6 oxygen ions). In the spinel cubic structure (S.G.: Fd-3m, $a \sim 0.82$ nm) the interstitial sites are only partially occupied; metal ions occupy only one-eighth of A sites and one-half of B sites (Figure 1.5). According to the distribution of M^{2+} and Fe^{3+} ions over the interstitial sites, we differ between a normal and inverse spinel structure. In the normal spinel, the M^{2+} ions occupy the A interstitial sites and the Fe^{3+} ions occupy the B sites. In the inverse spinel, M^{2+} ions are distributed over B sites while Fe^{3+} ions are equally divided over the A and B sites. The general cation distribution over the structure can be represented as $(\text{Me}_x^{2+}\text{Fe}_{1-x}^{3+})[\text{Me}_{1-x}^{2+}\text{Fe}_{1+x}^{3+}]\text{O}_4$, where the round and the square brackets represent the tetrahedral sites and the octahedral sites, respectively. The factor x is also referred to as inversion factor ($x=0$ for normal spinel and $x=1$ for inverse spinel) [3].

Two different magnetic iron oxides, magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), display the spinel structure. The magnetite is an inverse spinel (structural formula: $(\text{Fe}^{3+})[\text{Fe}^{3+}_2]\text{O}_4$). Maghemite usually forms with oxidation of magnetite. The charge neutrality of the crystal after the oxidation of Fe^{2+} to Fe^{3+} is maintained by the formation of ionized vacancies at the octahedral sites (structural formula: $(\text{Fe}^{3+})[\text{Fe}^{3+}_{5/3}\square_{1/3}]\text{O}_4$, $\square$ stands for vacancy).

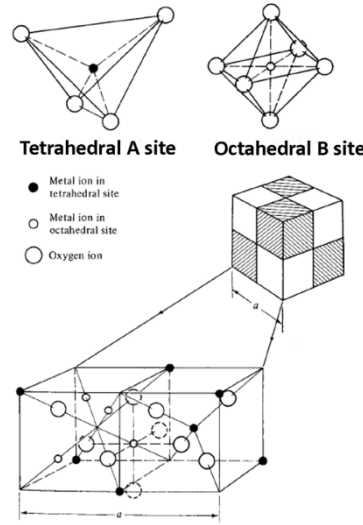


Figure 1.5: Spinel ferrite crystal structure [3].

The metal ions in the spinel structure interact through the oxygen atom with super-exchange interactions. The exchange integral J (Equation 1.7) in the cubic spinel structure is negative due to the antiferromagnetically coupled sublattices. The magnitude of the exchange energies between two metal ions depends on their distances between them and the angle M-O-M and it decreases in the following order: A-O-B > B-O-B > A-O-A. The overall magnetization in spinel cubic crystals is a result of the difference between the magnetization of total octahedral and tetrahedral lattices. Thus, the magnetic response depends on the type and the distribution of metal ions over the two interstitial sites. Basic structural and magnetic properties of some spinel ferrites are shown in Table 1.1 [3].

Table 1.1: Saturation magnetization M_s , anisotropy constant K_i , Curie temperature T_C and inversion factor x for some spinel ferrites [3, 22].

Ferrite	M_s (Am^2/kg)	K_i (10^4 J/m^3)	$T_C \text{ or } T_N$ ($^\circ\text{C}$)	x
Fe_3O_4	≈ 88	-1.4	585	1
$\gamma\text{-Fe}_2\text{O}_3$	≈ 85	-2.5	500-700	1
CoFe_2O_4	≈ 80	9	520	1
MnFe_2O_4	≈ 83	-0.28	300	0.2
ZnFe_2O_4	/	/	538	0

1.2.2 Hexagonal ferrites

Barium hexaferrite (HF) with a composition $\text{BaFe}_{12}\text{O}_{19}$ is representative of the M type hexaferrites. The hexagonal magnetoplumbite structure of M hexaferrites can be represented as a hexagonal stacking of close-packed layers of larger oxygen and barium ions with smaller iron ions positioned in interstitials. The structure can be subdivided into two alternating structural blocks stacked along the c-direction: a hexagonal R and a cubic S block (Figure 1.6). The hexagonal R block $(\text{BaFe}^{3+}_6\text{O}^{2-}_{11})^{2-}$ consists of three layers of oxygen atoms, where in the middle layer one oxygen is replaced with the barium atoms. The cubic S block $(\text{Fe}^{3+}_6\text{O}^{2-}_8)^{2+}$ consists of two close-packed oxygen layers and

three layers of interstitial irons. It is also called a spinel block, as it represents a (111) slice of the cubic spinel structure. The unit cell (S.G.: P63/mmc, $a = 0.588\text{nm}$, $c = 2.318\text{nm}$) can be presented by the RSR*S* stacking where the asterisk notes the rotation of the block for 180° around the hexagonal c-axis [23]. In the hexaferrite structure, the Fe^{3+} ions occupy five different crystallographic sites, i.e. tetrahedral ($4f_1$), octahedral ($12k$, $2a$, $4f_2$) and trigonal ($2b$) site [3, 24-27].

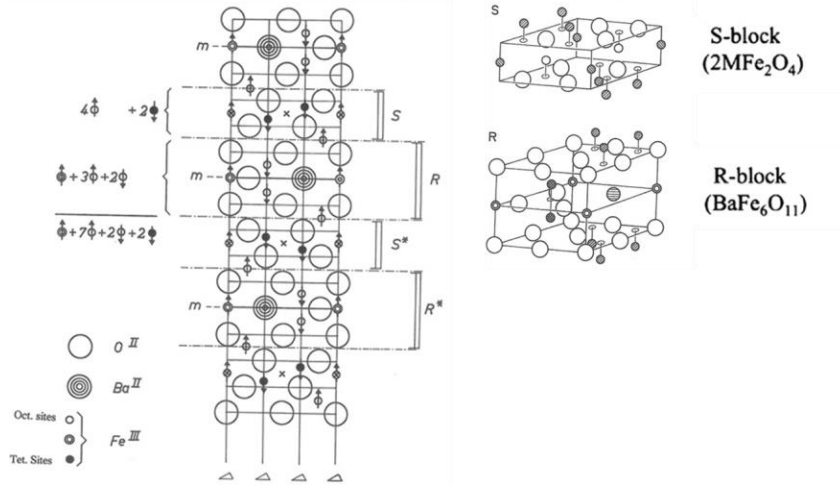


Figure 1.6: Magnetoplumbite hexaferrite crystal structure [3].

Barium hexaferrite contains large Ba ions, which causes a slight perturbation in the lattice dimensions, which results in a large magnetocrystalline anisotropy ($K_i = 3.3 \times 10^4 \text{ J/m}^3$ in the bulk). The hexaferrite has a preferred axis of magnetization along the c-axis. Therefore the magnetic properties are different if measured in parallel with the c-axis (M_s is reached with lower applied field and H_C is larger) than if measured oriented perpendicular to the field [24]. The magnetic moment of barium hexaferrite results from the sum of the magnetic moments in $12k$, $2a$ and $2b$ sites (spin orientation parallel to the c-axis) reduced by the moments in $4f_1$ and $4f_2$ sites (antiparallel spin orientation). Due to the differences of the oppositely oriented magnetic moments, barium hexaferrite exhibits a net magnetic moment of 40 Bohr magnetons. Basic magnetic properties of hexaferrite are shown in Table 1.2 [3, 25].

Table 1.2: Saturation magnetization M_s , anisotropy constant K_i , Curie temperature T_C and inversion factor x for some hexagonal ferrites with magnetoplumbite structure [3, 28, 29].

Ferrite	M_s (Am^2/kg)	K_i (10^4 J/m^3)	T_C or T_N ($^\circ\text{C}$)
BaFe₁₂O₁₉	≈ 72	33	450
SrFe₁₂O₁₉	≈ 67	0.38	459

1.3 Piezoelectricity and Ferroelectricity

Among 32 crystal classes, 11 possess a centre of symmetry – they are centrosymmetric and therefore do not possess polar properties. 20 of 21 non-centrosymmetric classes exhibit electric polarity when they are subjected to a stress. Such materials are called piezoelectric. Piezoelectricity is the ability of the material to convert mechanical energy into electric energy, or inversely, to deform mechanically under the application of an electric field. The origin of piezoelectricity is related to an asymmetry in the unit cell and resulting electric dipoles. When such material is exposed to a mechanical stress, a shifting of the positive and negative charge centres takes place, which results in an external electrical field. This is the direct piezoelectric effect. On the contrary, upon application of an electric field, an electrically induced force acts upon the ions, causing mechanical displacement of the ions which on a macroscopic scale reflects as geometric deformation.

Half of the piezoelectric crystal classes exhibit spontaneous polarization even in the absence of an electric field or mechanical stress. Polarization (dipole moment per unit volume) is a vector field that express the density of permanent or induced electric dipole moments in a material. A material exhibiting spontaneous electric polarization is visualized to be composed of negative and positive ions. In a certain temperature range, the centre of positive charge does not coincide with the centre of negative charge. Thus, each pair of positive and negative ions can be visualised as an electric dipole. The dipoles result in the occurrence of the spontaneous polarization due to an assembly of these dipoles, which point in the same direction. The electric dipole moment is a measure of the separation of positive and negative electrical charges in a material, that is a measure of the system overall polarity. 10 crystal classes with spontaneous polarization are said to be polar or pyroelectric. The direction of polarization of some pyroelectric materials can be changed by applying the electric field. Such materials are called ferroelectrics. Ferroelectrics contain a permanent electrical dipole at the unit cell level as a result of the non-symmetric crystal structure. The electrical dipole spontaneously aligns with those dipoles in adjacent unit cells to yield a net polarization. This process is analogue to the spontaneous alignment of magnetic moments observed in ferromagnetic materials. The defining characteristic of the ferroelectrics is that the direction of their polarization can be reversed by applying an electric field. The polarization varies non-linearly with the applied electric field and can be described by the P/E hysteresis loop which is analogue to the magnetic M/H hysteresis loop. As ferromagnetic materials, ferroelectrics have a transition temperature, called the Curie temperature T_c , where the spontaneous polarization vanishes and the material becomes paraelectric [30-32].

1.3.1 Bismuth titanate

Bismuth titanate (BIT) with a composition $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Figure 1.12.) is the representative of the Aurivillius-type compounds. Aurivillius compounds with general formula $(\text{Bi}_2\text{O}_2)[(\text{A}_{m-1}(\text{B})_m\text{O}_{3m+1})]$ consist of $(\text{Bi}_2\text{O}_2)^{2+}$ sheets alternating with $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ perovskite-like layers. The perovskite structure, named after the crystal structure of the mineral perovskite (calcium titanate, CaTiO_3) is the most important structure for ferroelectric materials. Perovskites have the general formula ABO_3 . In the perovskite structure the A-cation is coordinated by 12 oxygen ions. The B-cation is coordinated by 6 oxygen ions which form an octahedron. The structure can be seen as a build-up of corners sharing octahedra in the centre of which a large A-cation is positioned [31]. In the $(\text{Bi}_2\text{O}_2)[(\text{A}_{m-1}(\text{B})_m\text{O}_{3m+1})]$ formula of Aurivillius compounds, m represents the number of octahedra stacked along the direction perpendicular to the sheets, and A and B are the 12- and 6-fold coordination sites of the perovskite slab, respectively. This kind of

structure promotes plate-like morphology. At room temperature the symmetry of BIT is monoclinic, however, it is described with a simplified orthorhombic cell ($a = 0.511$ nm, $b = 0.5448$ nm and $c = 3.283$ nm) or even with a quasi-tetragonal cell. BIT is a ferroelectric material that has great potential for being employed as a high temperature piezoelectric because of its relatively high Currie temperature of 675 °C, high dielectric breakdown strength, low dielectric loss and strong anisotropy. Furthermore, BIT is one of the most important lead-free piezoelectrics [33-35]. In Table 1.3 basic properties of BIT are compared with properties of some common ferroelectric and piezoelectric materials.

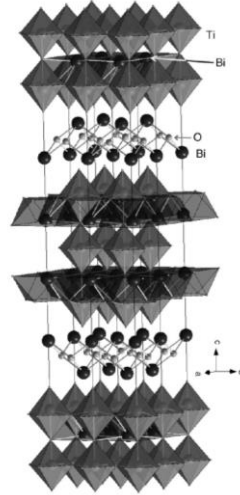


Figure 1.7: Schematic presentation of a crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [35].

Table 1.3: The piezoelectric coefficient d_{33} , relative dielectric constant ϵ , temperature T_C of some ferroelectric and piezoelectric materials [31, 34] .

	d_{33} (10^{-12} C/N)	ϵ (/)	T_C (°C)
$\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$ (PZT)	$\approx 250\text{-}700$	$1000\text{-}3800$	$165\text{-}360$
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT)	≈ 25	180	675
BaTiO_3	≈ 190	~ 1800	120

1.4 Synthesis of Nanoparticles

1.4.1 Precipitation

Precipitation is a process where soluble ions are transformed into a non-soluble solid phase with chemical reactions. The basic precipitation principles of the solid phase from liquid have been applied in a variety of technologies such as chemical technology, environmental science, biomedical research, etc. The precipitation has to be understood, in some cases because it needs to be avoided (e.g., sedimentation, mineralization of biological tissues), in other cases because it is a crucial part of synthesis. For example, synthesis of nanoparticles with wet-chemical methods usually requires a control of the precipitation.

The formation of the particles with precipitation is rather complicated, however it can be divided into four major steps [36, 37].

1.4.1.1 Formation of the zero-charged precursor

A solid phase is precipitated as a result of its supersaturation S caused by a chemical reaction. Basically, S represents the concentration of the solid product above its solubility in the liquid medium. It depends on the concentrations of the reactants and the kinetics of the chemical reactions forming the insoluble product. The formation of the insoluble product usually proceeds with a condensation (oleation or oxolation) of zero-charged precursor $[M(OH)_Z((OH)_2)_{N-Z}]^0$ which is formed with hydroxylation of the cation. The process is a very rapid acid-based reaction. Here, the supersaturation S will be defined as the ratio between the concentration of the zero-charged precursor in solution c_L and solubility of the solid product c_S [36]:

$$S = \frac{c_L}{c_S} \quad (1.13)$$

The formation rate of the insoluble product strongly depends on the way how it is formed. The formation could be promoted by the addition of the hydroxide to the cationic complex, thermal hydrolysis or by the thermal decomposition of a precursor [37].

1.4.1.2 Nucleation

Nucleation is an event where nuclei are formed through the condensation of the zero-charged precursor. Depending on the mechanism we can differ between homogeneous nucleation (HON), where three-dimensional nuclei are formed in the solution, and heterogeneous nucleation (HEN), where nuclei form on surfaces (e.g., of solid particles) present in the reaction mixture [36].

1.4.1.2.1 Homogeneous nucleation

Nucleation corresponds to the initial stages of the zero-charged precursor condensation and the consequent solid formation. Figure 1.8 schematically presents the whole precipitation process. In the Figure 1.8 a) changing of the precursor concentration with time is compared to changing of number and size of the precipitated solid particles. Graph b) shows changing of the nucleation rate and the growth rate with the precursor concentration in different stages of the precipitation process. At the start of the process, where the precursor concentration is low, the nucleation rate is zero. The precursor concentration increases monotonously with the time (zone I, Figures 1.8 a) and b)). First particles of the solid product start to form after the concentration of the precursor exceeds its solubility c_S . The probability of these particles to dissolve is higher than the probability for their growth, thus these meta-stable particles are referred to as embryos. With an increase in supersaturation their size grows and their free enthalpy decreases. When the particle reaches a critical size r^* , the probability of its growth equals the probability of its dissolution. The particle of the critical size represents the smallest stable particle in the system and is called nucleus. A change of free enthalpy, ΔG , which represents the energy required for the formation of the nucleus surface, can be expressed as:

$$\Delta G = -n \cdot k \cdot T \cdot \ln S + A \cdot \gamma \quad (1.14)$$

where n is the number of precursors, S is supersaturation, A is the surface area of the solid, and γ is the interfacial tension energy. The ΔG is related to the critical size of the nuclei through the supersaturation. The supersaturation significantly influences the critical size of nuclei which can be expressed with Equation 1.15. The size is defined at maximum ΔG and is smaller for higher supersaturation and smaller surface tension.

$$r^* = -2 \frac{\gamma}{\Delta G} \quad (1.15)$$

Note that the nucleus is not formed immediately after the concentration of the precursor exceeds the solubility of the solid product c_s . The nucleus is only formed when a critical concentration c_{min} is reached (beginning of zone II in Figure 1.8 a) and b)). At further increase of the supersaturation the nucleation rate rapidly increases and reaches maximum. The supersaturation increases until the formation rate of the precursor is higher than the condensation rate. After that the precursor concentration starts to decrease, usually because the precursor formation rate decreases due to a majority of reactants was already consumed. When the precursor concentration decreases below c_{min} , the nucleation stops (end of zone II in Figure 1.8 a) and b)) [37]. In parallel with the nucleation of new product particles in the zone II, the already formed nuclei grow. In the zone III (Figure 1.8) where the precursor concentration is below c_{min} only existing particles grow, while the nucleation rate is zero.

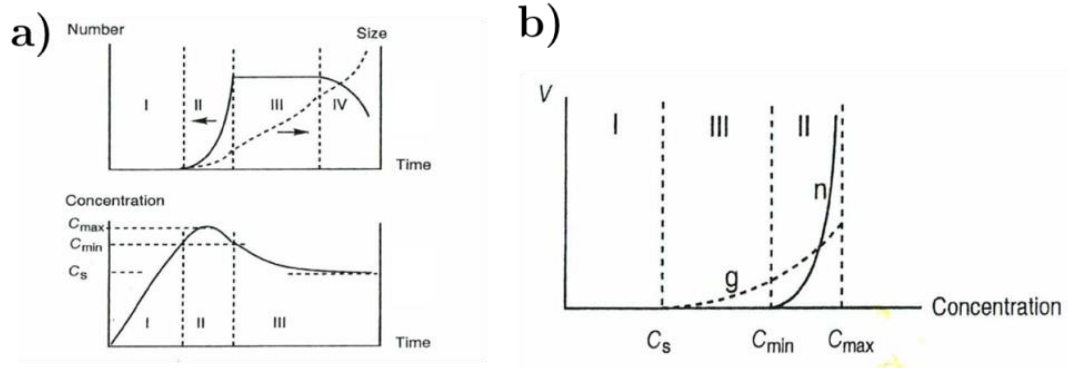


Figure 1.8: Change (a above) in the number and size of particles formed in the solution is compared with the change in the concentration c of the soluble precursor of the solid phase (a below) during the precipitation and (b) nucleation rate (denoted with n) and growth rate (denoted with g) as a function of the precursor concentration [37].

1.4.1.2.2 Heterogeneous nucleation

Heterogeneous nucleation (HEN) occurs on surfaces present in the precipitation medium, e.g., on particles of the foreign solid phase. The solid-solid interface energy is smaller than the solid-solution surface energy and since the ΔG is the function of γ (Equation 1.14), it decreases when nucleation proceeds at the surfaces. Because of the decrease of ΔG , nucleation on the surface of the present solid phase occurs more easily and the nucleation rate is increased. The nucleation rate can be expressed as:

$$J = B \cdot \exp\left(-f \frac{16 \cdot \pi \cdot v^2 \cdot \gamma^3}{3(k \cdot T)^3 \cdot \ln(1+S^2)}\right) \quad (1.16)$$

Where B is the constant, v is a particle volume, γ is the interfacial energy and parameter f describes the influence of the foreign particles on the nucleation barrier. On the basis of Equation 1.16, the HEN is energetically always more favourable at low S , while higher S promotes HON. As a result, the c_{min} is lower for the HEN compared to the HON. In the case when solid particles are present in the system, also the size, crystal structure and morphology of those particles need to be considered. Their presence can lead to more than one nucleation process and also different supersaturation levels in the same system. Moreover, the presence of foreign particles with structures related to the nucleating phase additionally lowers the energy barrier for the nucleation and allows epitaxial growth of the nuclei even at low supersaturation levels [37].

1.4.1.3 Growth

Growth of the nuclei that are formed during the nucleation process can be described as a sequence of five processes: (i) transport of ions through solution, (ii) adsorption at the crystal/solution interface, (iii) surface diffusion, (iv) reaction at the interface and (v) incorporation of the product into the crystal lattice. The nuclei grow with the addition of precursor molecules, which are still generated during the nucleation by chemical reactions. When the precursor concentration exceeds the c_{min} , nucleation starts, but in parallel the formed nuclei grow. The simultaneous processes of nucleation and growth generally result in a broad size distribution of the precipitated particles. When the c_L decrease below the c_{min} – usually because the reactants were consumed – the nucleation process stops, however, the particles keep growing until the c_L drops below the c_s (zone III in Figure 1.8 a) and b)).

For precipitation of particles with a narrow size distribution, the processes of nucleation and growth have to be separated. Namely, the nucleation rate should be much greater than the rate of precursor formation. If the nucleation rate is not high enough, the precursor concentration remains higher than c_{min} , and both processes occur simultaneously. In practice, the fast nucleation is achieved with an abrupt increase in the concentration of the reactants. If the chemical reaction is fast, the concentration of the zero-charged precursor rapidly increases to a high supersaturation, however it quickly decreases below the c_{min} , when the reactants are consumed [38].

1.4.1.4 Aging

Final step in the evolution of the particle, which determines its characteristics, is ageing. Particles obtained after the nucleation and growth steps are not necessarily thermodynamically stable. Aging takes place over a long period of time (hours, days), after all the reactants were consumed and the chemical reactions stop. It allows the system to reach its stability (zone IV in Figure 1.8 a) and b)). The stability of the system is usually reached in two ways. First, with increasing the particle size in a way that bigger particles grow at the expense of smaller particles. Increasing the particle size with the so-called secondary growth follows the laws of Oswald ripening. The energy of the system can also be lowered with recrystallization and morphology changes. During the precipitation process, the formation of crystals with various allotropes is possible. According to the Stranski rule, the least stable and the most soluble phase usually precipitate first. During the aging process particles can recrystallize into the more stable

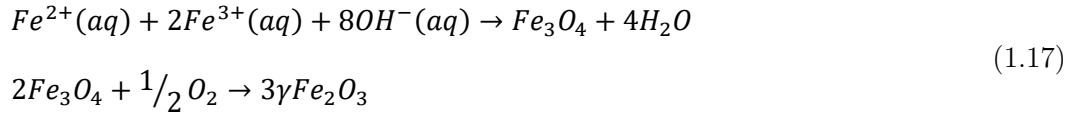
allotropic modification and amorphous phases could crystalize or change the morphology [37, 39].

1.5 Synthesis of the Spinel Ferrite Nanoparticles

Iron oxides with a spinel structure, magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (later referred to as spinel-ferrite) could be synthesized in a form of nanoparticles using numerous wet-chemical methods such as co-precipitation [40-43], microemulsions [44-46], sonochemical method [47], thermal decomposition [48-51], hydrolysis [52], hydrothermal synthesis [53-55], etc. All the mentioned methods enable some control over the nanoparticles' size and distribution. However, among the mentioned methods, the co-precipitation is probably the simplest and most efficient method for synthesis of spinel-ferrite nanoparticles.

Generally, the synthesis of the spinel-ferrite nanoparticles with co-precipitation proceeds with rapid addition of hydroxide (NaOH , NH_4OH etc.) into aqueous solution $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, which results in a high supersaturation of precipitating species [43, 56]. The Fe^{3+} ions are present in the aqueous solution in the form of hexaaqua $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions. At high temperatures, the Fe^{3+} hydrolyses already at relatively low pH values below $\text{pH} \sim 2$ to form iron (III) hydroxide ($\text{Fe}(\text{OH})_3$), which instantly transforms into the iron oxide-hydroxide (FeOOH). At room temperature, the acidic Fe^{3+} solution is stable. When the hydroxide is gradually added into the acidic solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, the Fe^{3+} precipitates first, already at low pH of ≈ 2.8 , whereas the Fe^{2+} precipitates at a higher pH of ≈ 5.6 . With the precipitation of Fe^{3+} FeOOH forms, first less-stable structural modification lepidocrocite ($\gamma\text{-FeOOH}$), which transforms into thermodynamically-stable goethite ($\alpha\text{-FeOOH}$) with growth of the $\gamma\text{-FeOOH}$ particles. The precipitating Fe^{2+} ions react with the FeOOH resulting in a spinel-ferrite formation. First, magnetite (Fe_3O_4) is formed, which usually oxidizes in air into maghemite ($\gamma\text{-Fe}_2\text{O}_3$). However, the precipitating Fe^{2+} ions will only react with the FeOOH when it is in the form of $\gamma\text{-FeOOH}$. If the process is slow, some secondary phases are formed because the $\gamma\text{-FeOOH}$ partially transforms in $\alpha\text{-FeOOH}$. The $\alpha\text{-FeOOH}$ cannot react with Fe^{2+} to form the spinel ferrite, but can transform to non-magnetic iron oxide hematite ($\alpha\text{-Fe}_2\text{O}_3$). The nanoparticles are therefore usually synthesised with a rapid addition of the hydroxide, which results in instant formation of the spinel ferrite.

The spinel formation proceeds according to the following overall chemical reactions, which is also known as the Shikorr reaction [22, 40, 57].



The synthesis of the spinel ferrite with co-precipitation proceeds under conditions of very high supersaturation of precipitating species, which result in a rapid burst of nuclei. The process is very fast, which limits its control. Depending on the synthesis conditions the sizes of the synthesized nanoparticles can vary from a few nanometres to micrometres.

1.6 Synthesis of Bi-Magnetic Nanoparticles

Bi-magnetic composite nanoparticles usually display a core-shell (CS) structure. It was found that the strongest exchange coupling could be reached with the CS structure due to the largest contact area between the phases compared to the other heterostructures

[14]. The CS structure is also beneficial from the viewpoint of controlling the structure of the composite nanoparticles.

The magnetic materials that are used for bi-magnetic nanoparticles include metals (Fe, Co, Cr, Ni, Pt) [58-62], alloys (FePt and CoPt) [14, 62-64], carbides (Fe_3C , Ni_3C) [60, 65], simple oxides (antiferromagnetic FeO, MnO, CoO) [64, 66-68] and mixed oxides. Frequently used simple oxides for bi-magnetic composites are spinel ferrites, with cobalt ferrite (CoFe_2O_4) [12, 13, 67-70] as the only hard-magnetic one among spinel ferrites and numerous soft-magnetic representatives such as magnetite (Fe_3O_4) [14, 63, 69], maghemite ($\gamma\text{-Fe}_2\text{O}_3$) [61, 62], nickel ferrite (NiFe_2O_4) [17], manganese ferrite (MnFe_2O_4), [13, 70] and zinc ferrite (ZnFe_2O_4) [12].

The CS structured bi-magnetic nanoparticles can be synthesized with co-precipitation [71, 72], thermal decomposition [11-14, 63, 70, 73], reduction and oxidation of metal nanoparticles [12, 74, 75] etc. One of the simplest methods to form CS nanoparticles is surface treatment of the nanoparticles. In this method, the shell is formed by oxidation or reduction of the core nanoparticles. However, despite its simplicity it has many drawbacks: (i) the shell is always formed from the core, consequently the size of the core and the shell cannot be independently controlled; (ii) since the shell phase has to be formed with surface treatment of the core material, the possible variations of the core/shell phases are limited; (iii) since the materials in the core and the shell often have quite different structural characteristics (e.g., metal vs. oxide), the structural quality of the shell may be inferior.

Another approach for synthesizing the CS bi-magnetic nanoparticles is the seed-mediated method. This method is based on the two-step process which maximizes the control over the size of the core and thickness of the layer. In such a sequential method, pre-synthesized core nanoparticles are coated with a shell in the following coating step. The size of the core and the thickness of the shell can be closely tuned with varying the experimental conditions in each step separately. Usually the synthesis proceeds with thermal decomposition of organometallic precursors (e.g. metal benzoylacetate, acetylacetate and metal oleates) in high boiling point solvents (e.g. octadecanol, hexadecandion) and in the presence of capping agents (e.g. oleic acid, oleylamine) [11-14, 63, 70, 73]. With this method it is possible to synthesize mono-disperse composite nanoparticles, which are dispersible in a non-polar media. However, the CS nanoparticles prepared with thermal decomposition can have diffuse interfaces between the two magnetic phases, which could decrease the exchange coupling effect. Moreover, the drawback of the method is also its complexity and the use of toxic and expensive starting reagents and high temperatures.

1.6.1 Deposition of the spinel-ferrite shell using controlled co-precipitation method

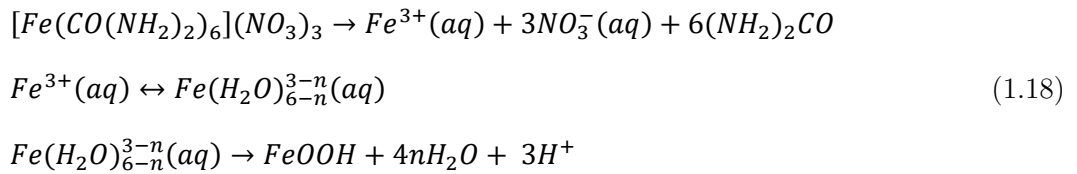
The co-precipitation is a widely used method for synthesis of the spinel-ferrite iron oxides. Furthermore, this method could also be used for the synthesis of CS nanoparticles with a deposition of the spinel-ferrite shell on the surfaces of core nanoparticles.

Composite nanoparticles composed of a magnetic spinel-ferrite shell deposited onto core nanoparticles can be synthesized with simple, low-temperature co-precipitation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions in the aqueous suspension of core nanoparticles. This controlled co-precipitation method was successfully used for the deposition of soft-magnetic maghemite layers on surfaces of hard-magnetic barium hexaferrite nanoparticles [72, 76]. Because this method was used in for synthesis of CS nanoparticles this work, it will be described in detail.

The spinel-ferrite shell is formed in a sequence of the chemical reactions and transformation. As explained in Chapter 1.5 the chemistry of the precipitation is quite complex and depends significantly on the reaction conditions (temperature, the reactant concentration, presence of the counter ions etc.) [22]. To form the spinel-ferrite shell, the precipitating species should heterogeneously nucleate and grow on the surfaces of the core nanoparticles. To enable exclusive heterogeneous nucleation of the product during the precipitation, the supersaturation of the precipitating species should be closely controlled (see Chapter 1.4.1.2 for theoretical background of the nucleation). The supersaturation level should be high enough for the heterogeneous nucleation to proceed, however below the level required for the homogeneous nucleation. As the ionic chemical reactions in aqueous suspensions are very fast and the supersaturation depends mainly on the concentration of the reactants. However, it is very difficult to maintain the concentration of the reactants constant throughout the whole reaction mixture, even the mixing is very intensive [36]. Additional problem occurs when controlling the supersaturation during the co-precipitation of two cations precipitating at different pH values. Such problem is also with the two iron ions – the Fe^{3+} precipitate at $pH \approx 2.8$ and the Fe^{2+} at $pH \approx 5.6$.

To ensure the controlled release of the reactants enabling the low and controlled supersaturation, the reactive Fe^{3+} ions were immobilized into a nitrate complex with urea $[Fe((H_2N)_2C=O)_6(NO_3)_3]$ (later Fe-urea complex) [51]. The immobilization of the Fe^{3+} ions into the complex not only enables the controlled release of the iron ions homogeneously into the suspension, but also postpones the precipitation of the Fe^{3+} ions to higher pH values, closer to the pH of Fe^{2+} precipitation, thus enabling the almost simultaneous precipitation of the two iron ions. The process of spinel-ferrite shell formation can be divided into three stages:

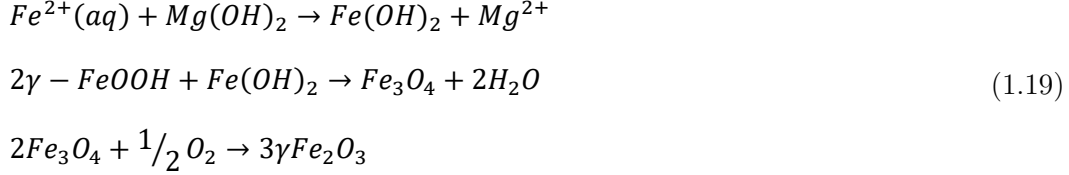
In the first stage, the stable aqueous suspension of the core nanoparticles containing the Fe-urea complex and Fe^{2+} ions was maintained at elevated temperature (usually 60 °C) for some incubation time (usually 10 minutes), needed for the thermal decomposition of the complex. The released Fe^{3+} ions in the aqueous media form hexa-aqua ions $[Fe(H_2O)_6]^{3+}$, which hydrolyse at the elevated temperatures to iron-oxide hydroxide ($FeOOH$). The decomposition of Fe-urea complex can be described with the following chemical reactions:



It was shown that the first phase that was formed during the complex decomposition was lepidocrocite (γ - $FeOOH$), which further transforms into the magnetic spinel iron oxide when it reacts with the Fe^{2+} ions. The formed γ - $FeOOH$ is only stable for very small particles (below 5 nm), where the decreased surface enthalpies for hydration increase the thermodynamic stability of γ - $FeOOH$. However, with prolongation of the incubation time or with the increased reaction temperature the γ - $FeOOH$ transforms into unwanted goethite (α - $FeOOH$), which can only transform further into non-magnetic hematite (α - Fe_2O_3) [22].

After the incubation time needed for the thermal decomposition of the complex and the thermal hydrolysis of the released Fe^{3+} ions, a solid precipitating agent ($Mg(OH)_2$) is added into the reaction mixture. With slow dissolution of $Mg(OH)_2$, the hydroxyl ions are homogeneously released into the reaction mixture resulting in a slow increase of the pH.

The second stage of the spinel layer formation process starts when the pH reaches value ≈ 5.6 resulting in the precipitation of Fe^{2+} ions. In the second stage, the precipitated Fe^{2+} ions react with $\gamma\text{-FeOOH}$ phase resulting in its transformation to spinel ferrite according to the following reaction:



The transformation with structural rearrangements is initiated with the adsorption of Fe^{2+} ions on the $\gamma\text{-FeOOH}$ surface. The $\gamma\text{-FeOOH}$ to spinel transformation proceeds with the dehydration and the local structural rearrangement, initiated by the precipitated Fe^{2+} species.

In the third, final stage of the spinel-ferrite shell formation, the reaction mixture is maintained at the final pH. At that stage the transformation from $\gamma\text{-FeOOH}$ to spinel is completed [76].

1.7 Colloidal Suspensions

Colloid is a system of two separate phases. Typically it contains small solid particles (1 nm – 1 μm in size) which are dispersed in the carrier liquid. Due to complexity, the system cannot be treated as an exact problem but its understanding is interdisciplinary in nature. The factors that contribute to the behaviour of colloidal system are particle size, shape and flexibility, surface properties, particle-particle and particle-solvent interactions. Additional factor playing an important role in the suspension behaviour is also large contact area between the particle and the medium [77].

1.7.1 Inter-particle forces

The forces that act between the particles in the suspension can be divided into two groups: long- and short-range forces. The short-range forces usually act in a range compared to the distance of a molecular/particle contact (< 1 nm), while the long-range forces can influence the particles on distances of up to 100 nm. The interaction energy depends on the force that decreases with the increasing distance between the two particles l . For example, a short-range Van der Waals (VDW) force decreases with the sixth power of the distance between particles (l^6), while a long-range Coulomb interaction force decreases with l^2 [78].

The forces between the particles in the suspension can be defined as attractive or repulsive forces. The attraction/repulsion between two particles strongly depends on the nature of the particles and on the properties of the medium. For example, in the case of the magnetic nanoparticles the attraction forces acting between them are VDW and dipole-dipole magnetic forces.

The repulsion between the particles in a colloidal suspension could be obtained via electrostatic, steric, electrosteric or solvation forces [77, 78]. With careful control of inter-particle forces, colloidal suspension can be prepared in the dispersed, weakly flocculated, or strongly flocculated or agglomerated states. Colloidal stability depends on the inter-particle energy, E_{total} , which can be expressed as:

$$E_{total} = E_{VDW} + E_{elect} + E_{steric} + E_{struct} \quad (1.20)$$

where E_{VDW} is the attractive potential due to the short-range VDW interactions between particles, E_{elect} the repulsive potential energy resulting from electrostatic interactions between particle with the same sign of the charge, E_{steric} the repulsive potential energy resulting from steric interactions between particle surfaces coated with surfactants and E_{struct} the potential energy resulting from the presence of non-adsorbed species in solution that may either increase or decrease suspension stability. The first two terms in the Equation 1.20 are presented in the theory developed by Derjaguin, Landau, Verwey and Overbeek (the DLVO theory), which predict the stability of colloidal particles suspended in a polar solution [79].

1.7.1.1 Van der Waals (VDW) forces

Van der Waals forces result from the dipole or induced-dipole interactions between the two atoms. The model bases on mutual effects of positive and negative charges of the neighbouring atoms A and B. Electrons from atom A repel those in the atom B but at the same time they attract the positively-charged nucleus of atom B, and oppositely (Figure 1.9 a) and b)). Attraction and repulsive forces are in equilibrium but only to the distance of ≈ 0.4 nm [80].

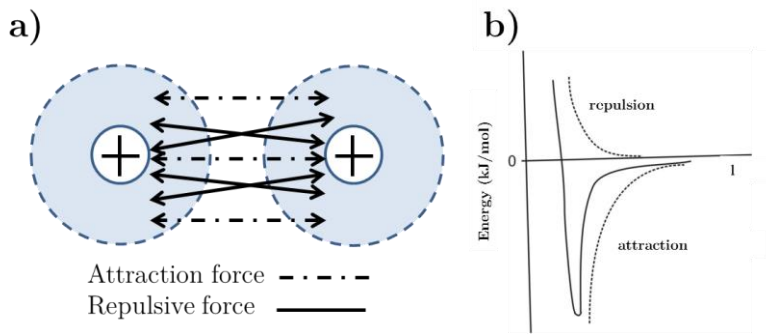


Figure 1.9: Model of the VDW attraction forces a) and energy of the VDW forces between two atoms b) [80].

Van der Waals potential energy (E_{VDW}) between the particles exhibits a power-law distance dependence whose strength depends on the dielectric properties of interacting colloidal particles and medium. For the same-size spherical particles, E_{VDW} is given by the Hamaker expression:

$$E_{VDW} = -\frac{A_H}{6} \cdot \left(\frac{2}{s^2-4} + \frac{2}{s^2} + \ln \frac{s^2-4}{s^2} \right) \quad (1.21)$$

where s is expressed as:

$$s = \frac{2a+h}{a} \quad (1.22)$$

and where h is the separation between the particle surfaces, a is the particle radius and A_H is the Hamaker constant. To achieve the desired degree of suspension stability the attractive VDW forces between the particles should be overcome. The attraction forces

have to be opposed by some type of repulsive forces, such as electrostatic or steric repulsive forces [78, 79].

1.7.1.2 Electrostatic forces and DLVO theory

Colloidal stability of the particles in the polar solvents can be controlled by generating electrostatic forces between particles. The repulsive electrostatic energy between two particles exhibits an exponential distance dependence whose strength depends on the surface potential induced in the interacting colloidal particles and the dielectric properties of the medium [79]. Particles suspended in polar media are usually charged. The charging of the particles' surface can arise by the ionization or dissociation of surface groups or by the adsorption of ions from solution onto a previously uncharged surface. During the charging mechanism, the ions with the opposite charge as the surface (counter ions) are attracted toward the surface and those with the same charge (co-ions) are repelled by the surface. The charge surface and neutralizing excess of counter-ions over co-ions distributed close to the surface leads to the formation of the electric diffuse double layer. Stern proposed a model in which double layer is divided into two parts; Stern and diffuse layer (Figure 10 a)). In the Stern layer the ions are adsorbed/attached to the surface by electrostatic and/or VDW forces while those who are not attached are located in the diffuse layer which is separated from the Stern layer by a Stern plane. In the double layer, the potential changes from the ψ_o (surface potential) through the ψ_d (the Stern potential) in the Stern layer further to 0 in the diffuse region of the double layer (Figure 10 b)). ψ_o can be estimated from the electrokinetic measurements. Electrokinetic behaviour depends on the potential at the surface of shear between the charged surface and the electrolyte solution. The potential is called the zeta potential (ζ -potential) [77, 78].

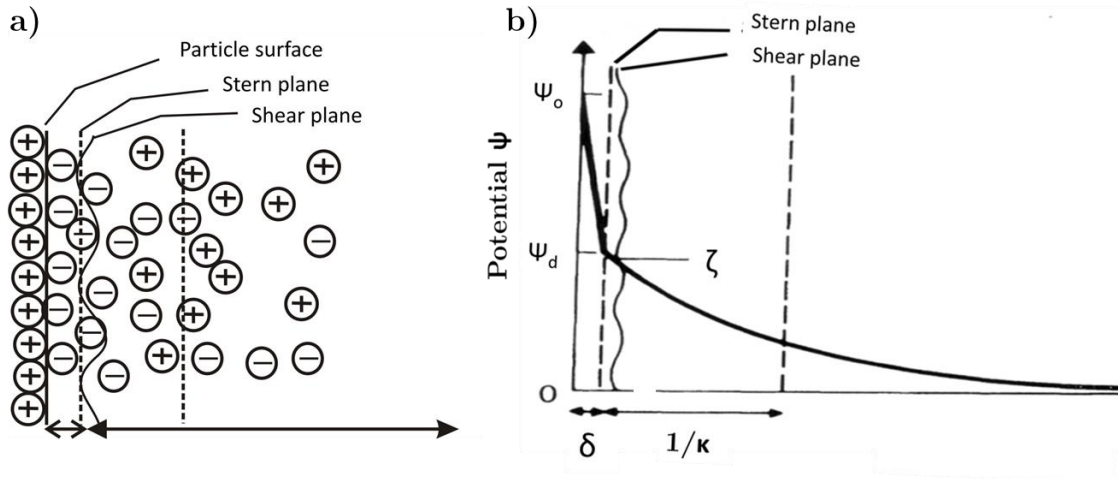


Figure 1.10: Schematic presentation of the structure of the electric double layer a) and change in the potential with the increasing the distance from the surface b)[77].

The Derjaguin-Landau-Verway-Overbeek (DLVO) theory of colloidal stability occupies a central position in the colloid science. According to this theory, the stability is predicted on the concept that two different forces govern the interaction between similar colloidal particles in polar solutions (Figure 1.11 a). It describes the relationship between the attractive VDW and repulsive electrostatic forces. For highly charged surfaces in dilute electrolyte, there will be strong long-range repulsion that peaks at some distance at the

energy barrier (Figure 1.11 c), curve a). If the concentration of electrolyte increased, the secondary minimum occurs before the energy barrier (Figure 1.11 b). At this point the particles are reversibly flocculated (Figure 1.11 b), curve b and Figure 1.11 c), curves b, c and d). With increasing the electrolyte concentration (increased ionic strength and decreased double layer) or with changing the pH toward the isoelectric point (IEP), the energy barrier decreases (Figure 1.11 c), curves b, c and d). With lowering the energy barrier, the electrical double layer repulsion gets smaller and the surface charge approaches to zero. At this point the interaction curve approaches to the pure VDW curve and the two surfaces now attract each other at separation distances (Figure 1.11 c), curve e). Particles are in a primary minimum and they are irreversibly agglomerated [78, 81].

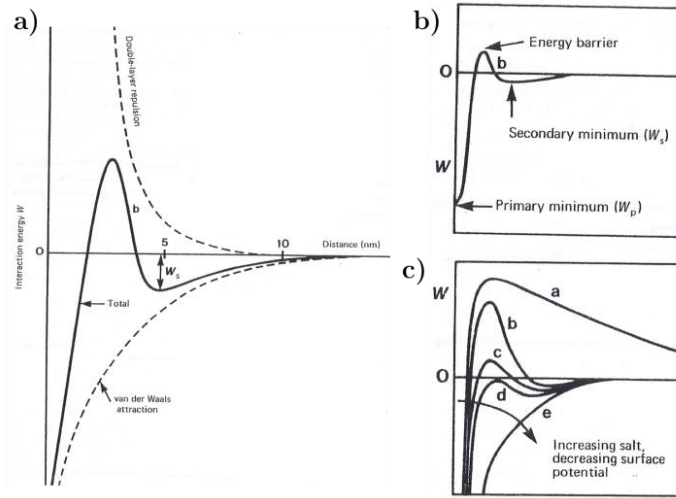


Figure 1.11: Energy versus distance profiles of DLVO interactions a), example of a secondary minimum as a consequence of electrostatic interactions b), and total interaction in dependence on the ionic strength and surface potential c) [78].

1.7.1.3 Steric forces

An alternative route to control the colloidal stability of the particles is with steric stabilization. In this approach, adsorbed organic molecules (usually polymers) are utilized to induce steric repulsions. For effective steric repulsions, the adsorbed layer must be thick and dense enough to overcome the VDW attraction forces between the particles and to prevent the bridging flocculation. Steric interaction occurs when particles approach one another at separation distance less than twice the thickness of the surfactant layer [79].

1.7.1.4 Electrosteric forces

Polyelectrolytes are species that can provide electrostatic and steric stabilization to a given colloidal dispersion. Such system is referred to as electrosterically stabilized. Polyelectrolytes contain at least one type of ionisable group (e.g. carboxylic or sulfonic group) and they could be in the form of homo-polymers (polyacrylic acid) or block copolymers with one or more ionisable segments. Adsorption of the species is strongly influenced by the chemical and physical properties of the solid surfaces and solvent medium. The adsorption of the polyelectrolyte species is favoured when the species

possess an opposite charge than the colloid surfaces. Thus the adsorption behaviour and conformation of polyelectrolyte species can be modulated by tailoring solvent parameters (e.g. pH and ionic strength) [79].

1.7.1.5 Solvation forces

With decreasing the separation distances below the few molecular diameters (σ), the structure of the fluid molecules which intervene with particles surfaces can play a role.

Forces that are a consequence of the crowding of the solvent molecules, very near the particles' surfaces, are referred to as solvation, structural or in the case of the aqueous medium hydration forces. The solvation/hydration forces arise once there is a change in the liquid density between the two approaching surfaces. For non-interacting particle surfaces the solvation forces are result of the changes in the molecular ordering and depends on the distances between particles, l (Figure 1.12 a)). Crowding of the molecules between the two surfaces causes pressure P which depends on the ionic density ρ at the surfaces (Equation 1.23).

$$P(l) = k \cdot T[\rho_s(l) - \rho_s(\infty)] \quad (1.23)$$

When l is a multiplier of molecular diameter (σ), the ionic strength is high but should decrease in some intermediate separation distances. For the large separation distances, ionic density approaches the values for the isolated surfaces ($\rho_s(\infty)$) where the solvation pressure approaches zero. Variation of the solvation pressure with distance results in an oscillatory nature of solvation forces (Figure 1.12. b)) [78, 82].

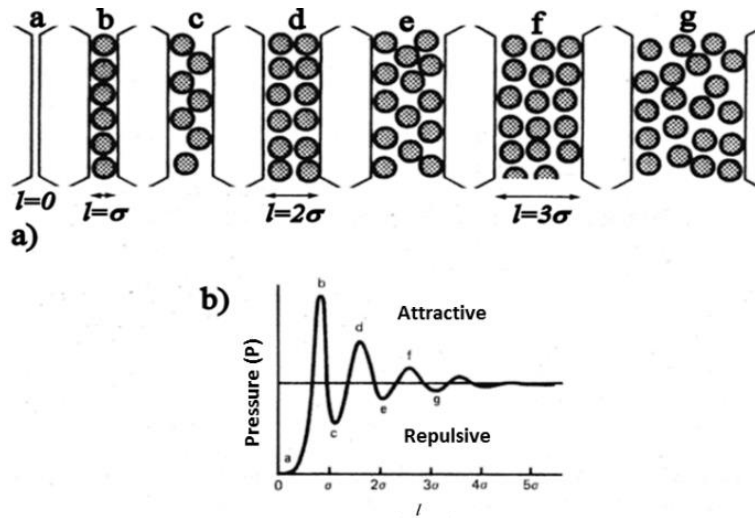


Figure 1.12: Distribution of the solvent molecules between the two approaching surfaces a), corresponding solvation pressure versus separation distance showing oscillatory nature of the solvation force b) [78].

1.7.1.6 Magnetic dipole-dipole interactions

Ferro/ferrimagnetic materials have a large tendency to agglomerate due to the dipole-dipole interactions. They describe the interactions of magnetic particles with the magnetic field induced by another magnetic particle. In a simple system of randomly

distributed nanoparticles the dipole-dipole interactions between the two neighbouring nanoparticles with the same size and same magnetic moment could be expressed by:

$$E_{dd} = -\frac{\mu_0 m_0^2}{4\pi l^3} \quad (1.24)$$

where m is the magnetic moment and l is the average separation distance. The interaction energy depends on several factors: (i) magnitude of the individual dipole, (ii) separating distances between acting dipoles, and (iii) on orientation of dipoles relative to each other.

The dipole-dipole interactions become negligible with decreasing the size below a superparamagnetic limit (usually below 20 nm). Below this size, the nanoparticles are in or are close to the superparamagnetic state. When they are in superparamagnetic state, they do not exhibit net magnetization, when the magnetic field is zero. Therefore there is no dipole-dipole magnetic interaction between the nanoparticles that would trigger their agglomeration. However, due to the large active surface, nanoparticles still have the tendency to agglomerate due to the attractive VDW forces which can be suppressed with applying high/strong steric and/or electrostatic repulsion [5, 83].

Chapter 2

Aims and Hypothesis

The purpose of this dissertation was to develop new knowledge about chemistry and mechanisms enabling the controlled synthesis of the composite nanoparticles with deposition of a shell of magnetic spinel iron oxide onto different core nanoparticles. The method have already been used for synthesis of bi-magnetic nanoparticles coupling hard-magnetic hexaferrite cores with soft-magnetic spinel-ferrite shells. The basics of the method have already known, however, to exploit its full potential it should be further developed. The developed knowledge will enable close control of the shell thickness of the bi-magnetic nanoparticles. By controlling the shell thickness the saturation magnetization of the composite nanoparticles will be maximized and the shape of their magnetic hysteresis loop tuned for demands of specific applications. Moreover, the new knowledge will also be important to enable transfer of the same method for synthesis of entirely new composite materials by coating the magnetic shells onto other different core nanoparticles, for example, nanoparticles of other functional materials.

Because of their strong uniaxial magnetic anisotropy with an easy axis pointing perpendicular to the platelet, hexaferrite nanoplatelets make a foundation for different novel applications. However, the disadvantage is in relatively low saturation magnetization. According to my hypothesis the saturation magnetization of the nanoplatelets can be maximized with retaining the desired out-of-plane magnetization with deposition of the shell of magnetic iron oxide onto their surfaces. Moreover, the shape of the hysteresis loop of the composite nanoparticles can be tuned by varying the shell thickness. The composite nanoplatelets will magnetize as single-phase magnetic particles as long as the two components will be magnetically rigidly exchange coupled.

According to my second hypothesis the controlled co-precipitation method developed for the synthesis of the bi-magnetic composite nanoplatelets can be transferred to synthesis of entirely new materials if the iron-oxide shell will be deposited to the core nanoparticles of other functional materials, for example ferroelectric layered-perovskite bismuth-titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) nanoplatelets.

Chapter 3

Materials and Methods

3.1 Materials

For the synthesis described in my thesis, I have used the following reagents:

- Iron(III) nitrate hepta hydrate, Alfa Aesar
- Iron(II) chloride, Alfa Aesar
- Magnesium Hydroxide, Alfa Aesar
- Urea, Alfa Aesar
- Barium nitrate, Alfa Aesar
- Nitric (V) acid, Carlo Erba
- Hydrochloric acid, Carlo Erba
- Ethanol, 99.5 %, Carlo Erba
- NaOH, 98 %, Alfa Aesar
- Aqueous suspension of small anatase nanoparticles (approximately 4 nm in size) was the product of Cinkarna Celje (Slovenia)
- Recinoleic Acid, Alfa Aesar
- Bismuth titanate hydrate, 98%, Alfa Aesar
- Polyvinylpyrrolidone, Alfa Aesar
- Scandium nitrate, Alfa Aesar
- Ammonia hydroxide, 25 %, Carlo Erba
- Sucrose, Alfa Aesar
- Citric acid, 99 %, Alfa Aesar
- Tetra-ethylorthosilicate, 99%, Alfa Aesar

3.2 Methods

3.2.1 Synthesis methods

3.2.1.1 Basic procedure of controlled co-precipitation

The controlled co-precipitation of the spinel-ferrite nanoparticles was performed under the same reaction conditions as described in the literature [76], however without the presence of the core nanoparticles.

First, the reactive Fe^{3+} ions were coordinated with urea in $[\text{Fe}((\text{H}_2\text{N})_2\text{C}=\text{O})_6(\text{NO}_3)_3]$ compound using the procedure described in literature [84]. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.012 mol) was dissolved in 250 mL of ethanol. 0.1 mol of urea was dissolved in 100 mL of ethanol and added into the solution of iron ions. The mixture was intensively stirred at room temperature for 2 hours, resulting in a green precipitate of $[\text{Fe}((\text{H}_2\text{N})_2\text{C}=\text{O})_6(\text{NO}_3)_3]$

(Fe-urea complex). The precipitate was separated by filtering and washing with ethanol several times and finally dried at room temperature.

The procedure of controlled co-precipitation (later referred to as a “basic procedure”) proceeded as follows:

The iron precursors (Fe-urea complex (0.12 mmol) and FeCl_2 (0.09 mmol) were dissolved in 80 mL of distilled water, bubbled with argon and heated to 60 °C. To avoid the oxidation of the Fe^{2+} ions, the reaction mixture was continuously bubbled with argon. The solution of iron precursors remained at the final pH for an incubation time t_i of 10 min allowed for the thermal hydrolysis of the Fe^{3+} ions released from the Fe-urea complex. After the t_i , the $\text{Mg}(\text{OH})_2$ (0.32 mmol) was added into the solution resulting in an increase of the pH. After 2 hours at the final pH and temperature, the reaction mixture was cooled. The product was washed with distilled water for several times and prepared for further analysis.

To investigate the influence of the temperature and the duration of the complex decomposition on the controlled co-precipitation process, the experiments proceed as in the basic procedure, except that the temperature was varied between 50 and 70 °C and t_i was varied between 0 and 10 minutes.

For the evaluation of the influence of starting pH on the controlled co-precipitation process the experiments proceeded as follows: The Fe-urea complex (0.12 mmol) and FeCl_2 were admixed into the 80 mL of distilled water bubbled with argon. The initial pH of the solution was adjusted with the addition of 0.1 M aqueous NaOH to pH of 4 or 5. Then, the solution was heated to the final temperature of 45 °C or 50 °C. The solid $\text{Mg}(\text{OH})_2$ (0.32 mmol) was added into the reaction mixture, when the mixture reached the final temperature ($t_i = 0$) or after 10 minutes ($t_i = 10$ min). After 2 hours at the final temperature and pH, the reaction mixture was naturally cooled to the room temperature and the product was thoroughly washed with distilled water.

The influence of the starting pH on the controlled co-precipitation process was also investigated under reductive conditions. To enable the reductive conditions, 0.03 mol hydrazine (N_2H_4) was added in the aqueous solution together with the iron precursors.

3.2.1.2 Synthesis of composite nanoparticles

3.2.1.2.1 Synthesis of hexaferrite core nanoplatelets

Sc-doped barium hexaferrite nanoparticles (BSHF) with a nominal composition $\text{BaFe}_{11.5}\text{Sc}_{0.5}\text{O}_{19}$ were synthesized using a hydrothermal method [85, 86]. Metal nitrates (4.16 mmol Ba^{2+} , 18.2 mmol Fe^{3+} , 2.6 mmol Sc^{3+}) were dissolved in 200 mL of distilled water and precipitated when added in 200 mL of aqueous NaOH solution (1.13 mol). The suspension of precursors was sealed in an autoclave and heated to 240 °C. Immediately after the autoclave reached the final temperature the autoclave was naturally cooled to room temperature. The product was washed with diluted nitric acid (to dissolve barium carbonate (BaCO_3) that could form due to the excess of Ba) and with distilled water. After the purification, the product was re-dispersed in water at $\text{pH} \approx 4.7$. According to the ζ -potential measurements, the suspension of BSHF nanoparticles exhibits the largest positive surface charge at this pH. High ζ -potential results in strong electrostatic repulsive forces that enabled the preparation of the stable aqueous suspension.

3.2.1.2.2 Synthesis of bismuth titanate core nanoplatelets

Another type of nanoparticles used as cores was bismuth titanate (BIT) nanoplatelets. The BIT ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) nanoplatelets were synthesized with hydrothermal method [87]. First the 6 mmol of bismuth nitrate were dissolved in 20 mL of distilled water with addition of 4 mL of concentrated HNO_3 . When bismuth nitrate was dissolved the anatase nanoparticles (8 mmol of Ti^{4+}) were added as the titanium precursor. The Ba^{2+} ions were precipitated with the addition of 156 mmol of aqueous NaOH. The reaction mixture was sealed in a Teflon autoclave and treated for 24 hours at 200 °C. After cooling, the product was washed with distilled water.

3.2.1.2.3 Deposition of maghemite layers onto the hexaferrite core nanoplatelets

The BHSF nanoplatelets were dispersed in water at the pH of 4.7. The suspension (80 mL) containing the core nanoparticles (0.05 mmol) was heated to 60 °C under argon flow to expel dissolved oxygen. The amount of core nanoparticles was estimated according to their surface area. The core nanoparticles displayed the surface area of $\approx 5.5 \text{ m}^2$, similar to the core used in previous successful syntheses [72, 76]. Then, the Fe-urea complex and FeCl_2 were added into the suspension of the core nanoparticles. The concentration of the added Fe precursors was varied in order to control the thickness of the formed maghemite layer deposited on the core nanoplatelets. With varying the concentration of the Fe-urea complex from 0.09 mmol to 0.18 mmol and FeCl_2 from 0.045 to 0.09 mmol the ratio between the Fe precursors and the BSHF nanoplatelets (the M/HF ratio) varied from 2.7 to 5.4, respectively. Due to the dissolution of the Fe precursors, the pH of the suspension decreased to ≈ 2.2 . The suspension was mixed at the final temperature for the incubation time t_1 of 10 minutes to allow hydrolysis of the Fe^{3+} ions released by slow thermal decomposition of the Fe-urea complex. Then, the solid $\text{Mg}(\text{OH})_2$ (from 0.24 mmol to 0.48 mmol) was added into the reaction mixture. The dissolution of the hydroxide resulted in a gradual increase of a suspension's pH needed for co-precipitation of the iron ions. After 2 hours at 60 °C, the reaction mixture was naturally cooled to the room temperature and the product was washed several times with distilled water.

To increase the thickness of the spinel layer at the core nanoparticles, the coating process was conducted in two steps. The composite nanoparticles synthesized in the first step (M/HF= 5.4) were washed several times with diluted HNO_3 ($\text{pH} \approx 4$) to dissolve any $\text{Mg}(\text{OH})_2$, which remained in the product after the first step. After the purification, the initial composite nanoparticles were re-dispersed in water with $\text{pH} \approx 4.7$. The suspension of the composite nanoparticles exhibited large ζ -potential, however the suspension was not completely stable. To enable better colloidal stability of the system the agglomeration of the initial composite nanoparticles due to the magnetic dipole-dipole interactions was minimized by applying the surfactant polyvinylpyrrolidone (PVP) (2 g/L). The present PVP enable steric stabilization of the nanoplatelets. The synthesis of the spinel layer in the second step proceeded in the same way as described above. However, to maintain the low supersaturation of the precipitating species required for the heterogeneous nucleation, the concentration of the iron reactants was decreased compared to the first step (0.09 mmol Fe^{3+} and 0.045 mmol Fe^{2+}).

3.2.1.2.4 Deposition of the maghemite layer onto the bismuth titanate core nanoplatelets

The deposition of the iron oxide onto the BIT core nanoplatelets (sample FBIT) proceeded as in the case of the basic procedure used for the deposition onto the BSHF nanoplatelets ($n_{\text{Fe}^{3+}} = 0.18 \text{ mmol}$, $n_{\text{Fe}^{2+}} = 0.09 \text{ mmol}$). The concentration of the BIT core nanoparticles was determined to obtain the surface area of 5.5 m^2 .

3.2.1.2.5 Coating of the nanoplatelets with silica layer

The BSHF and BIT nanoplatelets were coated with silica using modified Stober process [88]. First 1.6 g of the citric acid was added into the 80 mL of aqueous suspension containing nanoplatelets (0.4 g). Then, the pH of the suspension was adjusted to 5.1 with 25% ammonium hydroxide. The suspension was heated to 80 °C and vigorously stirred. After 90 minutes at the final temperature, the suspension was cooled to room temperature. To remove the excess of the citric acid, the product was centrifuged and re-dispersed in a water/ethanol solution (volume ratio was 1:4) so that the concentration of the nanoplatelets was 0.5 g/L. To form the silica layer the 7.46 mM TEOS was added into the stable suspension of the nanoplatelets. The reaction was catalyzed by the addition of 1% of concentrated ammonium hydroxide and stirred overnight. The product was sedimented, washed, and re-dispersed in water.

To coat the composite nanoplatelets obtained by deposition of maghemite onto the hexaferrite nanoplatelets with silica, a low amount of the composites (≈ 10 mg) was dispersed into 20 mL of aqueous solution of sucrose with a concentration of 2.9 mol/L. Then, 40 μ L of TEOS and 100 μ L of EtOH was added into the suspension of the composite nanoplatelets. The coating reaction was catalyzed by the addition of 1% concentrated ammonium hydroxide and left stirred overnight. The product was sedimented, washed, and re-dispersed in water.

3.2.2 Characterization methods

3.2.2.1 X-ray powder diffraction

The phase composition of the samples was analyzed with X-ray diffraction (XRD). The XRD patterns were recorded using X-Ray diffractometer system Siemens D5000 with the CuK α radiation.

3.2.2.2 Electro-kinetic measurements

ζ -potential of the nanoparticles in their aqueous suspension was evaluated with electro-kinetic measurements. The measurements were done using Brookhaven Corp ZetaPALS Instrument. The pH of the suspension containing the nanoparticles was adjusted with 0.01, 0.1 and 1 M solution of NaOH and HCl.

3.2.2.3 Electron microscopy

For the transmission (TEM) and scanning-transmission (STEM) electron microscopy, the samples were suspended in ethanol and deposited on a copper-grid-supported lacy carbon foil. The TEM analyses were performed using a field-emission electron-source TEM JEOL 2010F equipped with an Oxford instruments ISIS300 EDXS detector operated at 200 kV. The detailed structural analysis of the BSHF and CNP nanoplatelets was performed with a probe Cs-corrected scanning transmission electron microscope (JEOL ARM 200CF STEM) operated at 80 kV. During analysis of the samples, high-angle annular dark-field (HAADF) and annular bright-field (ABF) detectors were used simultaneously at 68-180 and 10-16 mrad collection semi angles, respectively. To minimize the specimen drift, images were taken several hours after the insertion of the sample in the microscope and at least 20 minutes after the last sample positioning to minimize the goniometer drift. The chemical composition was analyzed using Jeol Centurio EDXS system with 100 mm² SDD detector and Gatan GIF Quantum ER Dual EELS system. The simulated HAADF STEM images of the BSHF and CNP platelets were calculated based on the atomic models for barium hexaferrite and maghemite and microscope

parameters using the quantitative STEM (QSTEM) code with a multi-slice method and frozen phonon approximation [89].

3.2.2.4 Magnetic measurements

The room temperature magnetic properties were evaluated using the vibrating sample magnetometer - VSM (Lake Shore 7307 VSM). The maximum applied field was 1 T. For magnetic measurements of the BSHF core and the corresponding composite nanoplatelets, a low amount of nanoplatelets was dispersed into a nonmagnetic sucrose matrix. The nanoplatelets (≈ 1 mg) were admixed into water (≈ 2 mL) under intense mixing. Then, 2 g of sucrose were dissolved in the suspension. The suspension was heated to 140 °C to melt the sucrose. The viscous suspension of the nanoplatelets was rapidly cooled to solidify. The solid was milled and uniaxially pressed into cubic compacts. Magnetization of the nanoplatelets-containing sucrose cubes was measured as a function of a magnetic field applied in three normal directions of the cube (along the pressing direction (x-axis), and perpendicular to the pressing direction (y-axis, z-axis) using VSM.

To show a clear difference between the hysteresis of the exchange-coupled composite nanoplatelets and the hysteresis of a physical mixture of the hard-magnetic and soft-magnetic phases, the mixture of BSHF and maghemite (M) nanoparticles was measured. To minimize the inter-particle interactions, both types of magnetic nanoparticles were dispersed in sucrose as described above. Then, the two magnetic-particles-containing sucrose powders were mixed together in an M/BSHF mass ratio of 1. The high-temperature magnetic measurements proceeded using the same device as was used for the room-temperature measurements. The measurements were conducted under an argon atmosphere and constant applied magnetic field 20 mT. The magnetization was measured at different temperature intervals with a heating rate of 5 °C/min with a 1 min settling time. The Curie temperature was calculated from the thermomagnetic data, by finding of its temperature derivate.

3.2.2.5 Raman spectroscopy

Raman spectra of the powdered samples of maghemite (M), barium hexaferrite core nanoplatelets (BSHF) and the composite nanoplatelets were recorded with Ramman spectrometer NT-MDR model Integra spectra for Materials Science equipped with a confocal microscope at room temperature. The 633 nm line of Helium-Neon laser was used as excitation. Scattered light was detected by cooled CCD camera 600 grooves/nm grating. Power density was approximately 5 mW. To obtain good signal-to-noise ratio and to prevent sample damage the first spectrum was acquired for 10 s, then the time was increased to 60 s and finally 10 spectra measured for 60 s were accumulated. Finally, the spectrum at the same position was acquired for 60 s. The same procedure was repeated at different locations and the spectra were compared. The spectra differ only in signal-to-noise ratios and absolute values of intensities. Positions of bands and relative intensities were always the same. For the interpretations spectra that were obtained by accumulating 10 spectra each acquired for 10 s were used, since they showed the best signal-to-noise ratio.

Chapter 4

Results

Basic principles governing the method for coating the core nanoparticles with a maghemite layer (later referred to as spinel-ferrite) were developed at a Department for Materials Synthesis of the Jožef Stefan Institute [72, 76]. It bases on the controlled co-precipitation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions and on heterogeneous nucleation of the precipitated products on the surfaces of the core nanoparticles in the suspension with weak hydroxide (the detailed procedure is described in Section 1.7.2) [76]. The heterogeneous nucleation of the product of precipitation at the core nanoparticles' surfaces in the suspension is of key importance for the formation of the homogenous, core-shell composite nanoparticles. Only the precipitating products heterogeneously nucleated at the core nanoparticles' surfaces will form the shell. If the precipitating products are homogeneously nucleated, they will form separate particles in the suspension. The heterogeneous nucleation will occur at a somewhat lower supersaturation of the products compared to the homogeneous nucleation. Generally, the supersaturation is defined by the kinetics of the precipitation reactions and the reactant concentrations, in our case on the concentration of Fe^{3+} , Fe^{2+} , and hydroxyl ions. As the ionic chemical reactions in water are very rapid, the supersaturation practically only depends on the reactant's concentrations. The crucial problem is to maintain the homogeneous concentration through the reaction mixture [39]. In the controlled co-precipitation method, the low and homogeneous supersaturation was enabled by the immobilization of the highly reactive Fe^{3+} ions into the coordination compound with urea $[(\text{Fe}(\text{CO}(\text{NH}_2)_2)_6)(\text{NO}_3)_3]$ (later referred to as Fe-urea complex). The controlled release of the Fe^{3+} ions was enabled by thermal decomposition of the complex. Moreover, the immobilization of the Fe^{3+} ions into the complex also solves another problem that is frequently observed in co-precipitation of two ions. Namely, the two ions generally precipitate at different pH resulting in a nonhomogeneous product. In our case, the Fe^{3+} ions precipitate at the pH around 2.8 and the Fe^{2+} ions at the higher pH, above pH = 5.6. The immobilization of the Fe^{3+} ions into the complex postpones their precipitation to the higher pH values, closer to the pH where Fe^{2+} ions precipitate. This enables the almost simultaneous precipitation of both iron ions.

Apart from the controlled release of the Fe^{3+} ions, the control over the supersaturation and homogeneity was also improved with a controlled release of the hydroxyl ions into the reaction mixture. Instead of using strong liquid hydroxide, a solid hydroxide $\text{Mg}(\text{OH})_2$ was used for the increase of the pH. The solid $\text{Mg}(\text{OH})_2$ displays low solubility in water, which increases with the temperature. The slow dissolution of the hydroxide particles results in the homogeneous release of the hydroxyl ions through the reaction mixture.

The controlled co-precipitation method was already successfully used for the synthesis of bi-magnetic nanoparticles combining hard-magnetic barium hexaferrite (HF)

nanoplatelet core covered with a soft-magnetic maghemite shell. In this work the method was adapted to enable the control of the shell thickness. It appeared that the composite nanoplatelets combining the hexaferrite core with the maghemite shell can be synthesized with incredible control. The detailed structural and magnetic characterization of the bi-magnetic nanoparticles is presented in Section 4.3.

I also tried to use the controlled co-precipitation method for deposition of the magnetic maghemite shells onto other core nanoparticles than hexaferrite. I tried to coat the maghemite also onto photocatalytic titania (anatase TiO_2) nanoparticles, magnetic manganite perovskite ($\text{La}_{0.53}\text{Sr}_{0.47}\text{MnO}_3$) nanoparticles, ferroelectric bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, later referred to as BIT) nanoplatelets, and some other core nanoparticles. It appeared that the method could not be directly transferred for the coating of any core nanoparticles in the suspension. The attempt of coating the maghemite onto the BIT core nanoplatelets is presented in Section 4.4. It appeared that under the same experimental conditions that were used for deposition of the maghemite onto the hexaferrite nanoplatelets, the maghemite shell could not be obtained. Moreover, the nanoparticles deposited on the surfaces of the BIT cores were amorphous.

The focus of this thesis is the question what is the reason for the large differences in between the deposition of the maghemite layers onto the hexaferrite and other nanoparticles. In the case of hexaferrite, the composite nanoparticles could be synthesized with an excellent controll. On the contrary, when other nanoparticles were used as the cores in the suspension, the shell of deposited iron oxide was frequently poorly crystalline or even amorphous.

The influence of the core nanoparticles on the formation of the spinel-ferrite shell can be ascribed to two different reasons.

The first reason can be related to the structural differences between the core and the spinel-ferrite shell. In the case of the HF core nanoplatelets, the structural similarity between the two structures at the interface results in low interface energy and in epitaxial growth of the spinel-ferrite layers on the HF basal surfaces [72]. In the case of other tested core nanoparticles the differences in the two structures are larger and do not generally enable the formation of the low-energy interfaces.

The second reason that can obstruct the crystallization of the deposited iron-oxide material at the core surface is of chemical nature. Partial dissolution of the core nanoparticles in the reaction suspension or chemical reaction of the cores with the reactants in the suspension could result in changes of the spinel-ferrite formation.

To answer this question, and as a result, to be able to change the process to enable successful deposition of the spinel-ferrite layer on different core nanoparticles, the basics of the controlled co-precipitation method were systematically studied. For that the experiments of the controlled co-precipitation were conducted in aqueous solution without the core nanoparticles. The experiments have been focused on the reaction parameters, which could favor the crystallization of the precipitated iron ions in the form of magnetic iron oxide. The results of this detailed study of the controlled co-precipitation method are presented in the next chapter, Section 4.1.

4.1 Synthesis of the Magnetic Spinel Iron Oxide Nanoparticles with Controlled Co-Precipitation

In our previous research it was shown that the spinel-ferrite shell could be deposited onto surfaces of core nanoparticles using simple controlled co-precipitation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions and heterogeneous nucleation and growth of the precipitating material at the surfaces. The deposition was successful when the spinel-ferrite shell was deposited onto the amorphous silica nanoparticles or on the hexaferrite nanoplatelets [72, 76]. However, later it was found that the same experimental conditions as were used for the deposition onto those two types of the core nanoparticles cannot be generally applied for the deposition of the spinel-ferrite shell onto any core nanoparticle. In this chapter the co-precipitation method was analyzed with a focus on the experimental conditions that can be applied to promote the crystallization of the magnetic iron oxide without changing the parameters, which are necessary for the formation of the shell at the core nanoparticles. The experiments were performed in the solution without the core nanoparticles, however, at conditions which will enable a low supersaturation needed for heterogeneous nucleation at the cores when present in the reaction mixture. At the controlled co-precipitation method the low supersaturation is maintained with slow thermal decomposition of the water-soluble Fe-urea complex. It was found that the Fe-urea complex starts to decompose at the temperatures above 45 °C [76].

During the controlled co-precipitation process the spinel-ferrite shell is formed in a sequence of chemical reactions and transformations. The process of forming the spinel-ferrite shell could be divided into three stages. In the beginning of the co-precipitation process, the stable aqueous suspension of the cores containing the Fe^{3+} -complex and the Fe^{2+} ions is maintained at elevated temperature for some period of time (the incubation time, t_i), needed for the thermal decomposition of the Fe-urea complex. Due to dissolved nitrate counter ions the suspension is acidic with a pH of approximately 2.2. Even though the suspension is acidic the Fe^{3+} ions, released from the complex, slowly thermally hydrolyze to form the $\gamma\text{-FeOOH}$. Due to slow release of the Fe^{3+} ions from the complex and due to their slow hydrolysis the supersaturation of the FeOOH is low promoting the heterogeneous nucleation on the core nanoparticles (if present). When the core nanoparticles are not present, such conditions result in the formation of relatively large, well crystallized (nano)particles. The reason for the formation of the large particles is in the low nucleation rate at the low supersaturation [37]. After the incubation time, typically of 10 minutes, the $\text{Mg}(\text{OH})_2$ is added into the reaction mixture. The addition of the hydroxide results in a gradual increase of the pH in the second stage (see Figure 4.1). When the pH reaches a value of approximately 5.6 Fe^{2+} ions start to precipitate. The Fe^{2+} ions react with initially formed $\gamma\text{-FeOOH}$ phase resulting in its transformation into the spinel ferrite. Considering the reaction conditions, the first spinel-ferrite phase, which occurs, is magnetite (Fe_3O_4). However, the nanosized magnetite will oxidize into maghemite ($\gamma\text{-Fe}_2\text{O}_3$) when exposed to ambient air. The pH is increased to the value necessary for the Fe^{2+} precipitation in about 5 minutes. Due to consumption of the hydroxyl ions with the precipitating Fe^{2+} ions, the rate of pH increase decreases, but pH keeps slowly increasing. After another 10 minutes the pH value settles at the value around 8. The product is aged for another 2 hours. In this final stage, the $\gamma\text{-FeOOH}$ to spinel transformation is completed.

The spinel is formed only if the $\gamma\text{-FeOOH}$, which results from thermal hydrolysis of released Fe^{3+} from the complex, reacts with precipitated Fe^{2+} ions. For spinel-ferrite formation with controlled co-precipitation, the Fe-urea complex should decompose at the optimum rate. Namely, the complex should decompose slowly enough for the majority of

Fe^{3+} ions to be released close to the pH value, where Fe^{2+} ions precipitate. This will enable simultaneous precipitation of both iron ions and the formation of spinel ferrite. The optimum decomposition rate of the Fe-urea complex also prevents the transformation of initially formed $\gamma\text{-FeOOH}$ into the unwanted $\alpha\text{-FeOOH}$, before it reacts with Fe^{2+} ions. Namely, the $\gamma\text{-FeOOH}$ is only stable in the form of very small nanoparticles. With time and/or temperature the $\gamma\text{-FeOOH}$ nanoparticles grow and at a certain size (around 5 nm) they transform to $\alpha\text{-FeOOH}$. The $\alpha\text{-FeOOH}$ does not react with the precipitating Fe^{2+} ions to form the spinel ferrite. Moreover, if the Fe^{2+} ions are unable to react with the $\gamma\text{-FeOOH}$ nanoparticles because they previously transformed to $\alpha\text{-FeOOH}$, they will oxidize and precipitate in the form of $\gamma\text{-FeOOH}$. Any $\gamma\text{-FeOOH}$ that will not react with the Fe^{2+} ions into the spinel ferrite will grow during aging and thus transform into the $\alpha\text{-FeOOH}$. The $\alpha\text{-FeOOH}$ is unable to form the desired spinel ferrite by the reaction with the Fe^{2+} ions, but it can further dehydroxylate into the nonmagnetic $\alpha\text{-Fe}_2\text{O}_3$ [76, 90].

4.1.1 Controlled co-precipitation using “basic” procedure

First, the controlled co-precipitation of the spinel-ferrite nanoparticles was performed under the same reaction conditions as were used in the case of the successful deposition of spinel-ferrite shell onto the hexaferrite nanoplatelets [72], however without the presence of the cores. The procedure, which will be referred to as a “basic” procedure later in the text, is as follows: The Fe-urea complex and Fe^{2+} ions were dissolved into water, heated to 60 °C and bubbled with argon, to expel any dissolved oxygen. After the incubation time of 10 minutes (t_i), allowed for the thermal hydrolysis of the released Fe^{3+} ions, the $\text{Mg}(\text{OH})_2$ was admixed into the solution. Figure 4.1 shows pH vs. time curve for the sample MNP-60-10, synthesized by this basic procedure. The pH value, required for the Fe^{2+} precipitation (pH ≈ 5.6) was reached in approximately 5 minutes, while the final pH of 7.2 was reached in approximately 15 minutes after the hydroxide addition (Figure 4.1). After 2 hours at final temperature and pH, the reaction mixture was cooled. The solid products were thoroughly washed with distilled water.

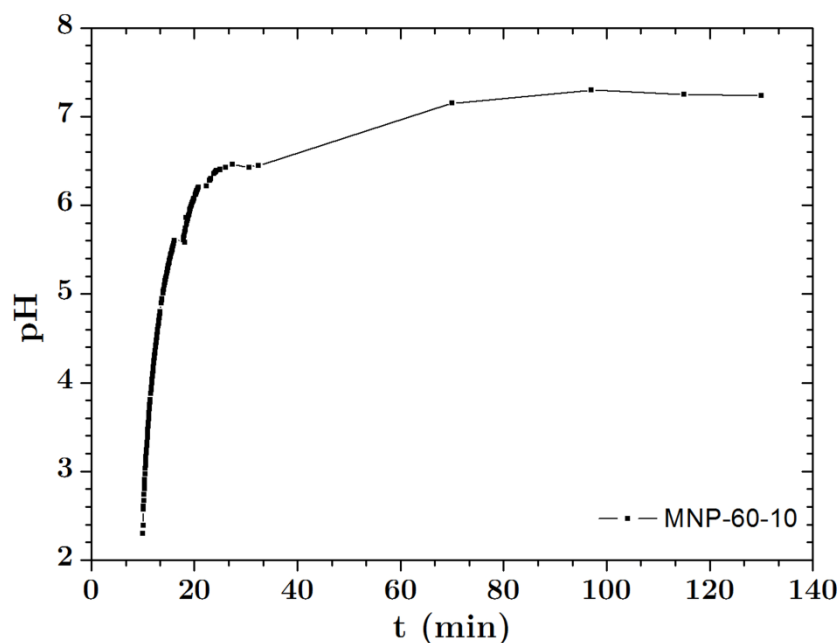


Figure 4.1: The increase of pH with time after $\text{Mg}(\text{OH})_2$ was admixed into the reaction mixture during preparation of sample MNP-60-10.

Figure 4.2 shows an XRD pattern of the sample MNP-60-10. The XRD pattern reveals peaks that can be indexed according to the cubic spinel structure. Additional peaks in the patterns can be indexed to an orthorhombic structure of $\text{Mg}(\text{OH})_2$, which appears as the impurity. The average crystallite size determined from the XRD diffraction peak broadening yields around 43 nm.

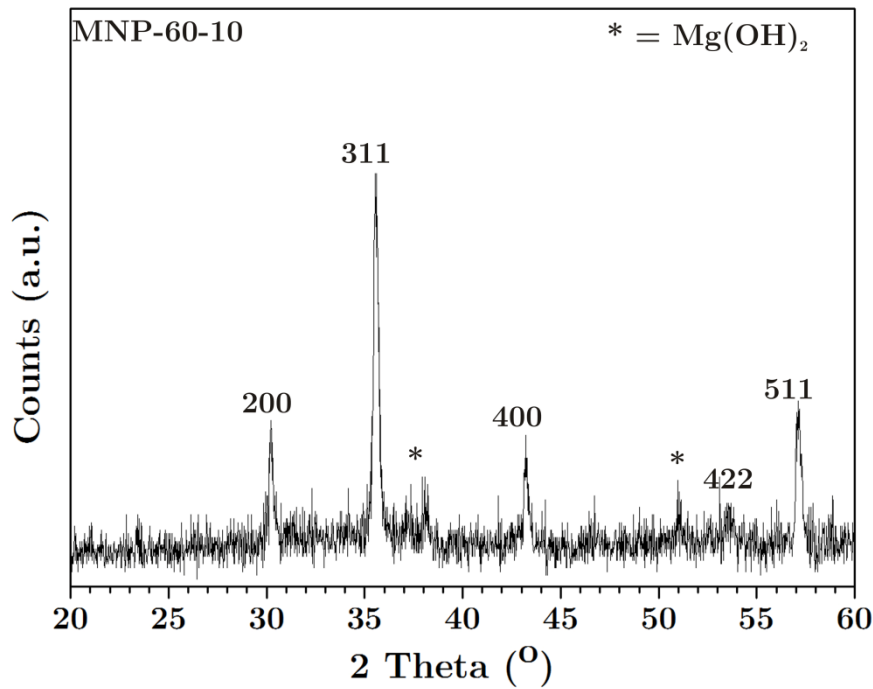


Figure 4.2: XRD pattern of the MNP-60-10 sample.

The product synthesized with the basic synthesis procedure was also investigated with the transmission electron microscopy (TEM). Figure 4.3 a) shows a representative TEM image of the sample MNP-60-10. The TEM revealed that the product contains two types of nanoparticles; small spherical nanoparticles and larger octahedral nanoparticles. The small spherical nanoparticles (Fig. 4.3. b)) were 5-10 nm in size. The selected area electron diffraction (SEAD) pattern taken from the area of the spherical nanoparticles reveals rings and spots that correspond to a hexagonal structure of α -Fe₂O₃ and orthorhombic structure of α -FeOOH. Figure 4.3 c) shows large octahedrally-shaped particles. The SAED pattern taken on the nanoparticle can be indexed according to the cubic spinel structure orientated along the [223] direction.

The secondary α -FeOOH and α -Fe₂O₃ phases could not be detected with the XRD due to their small size and poor crystallinity. They display broad peaks with low intensity which are below the background of the XRD pattern.

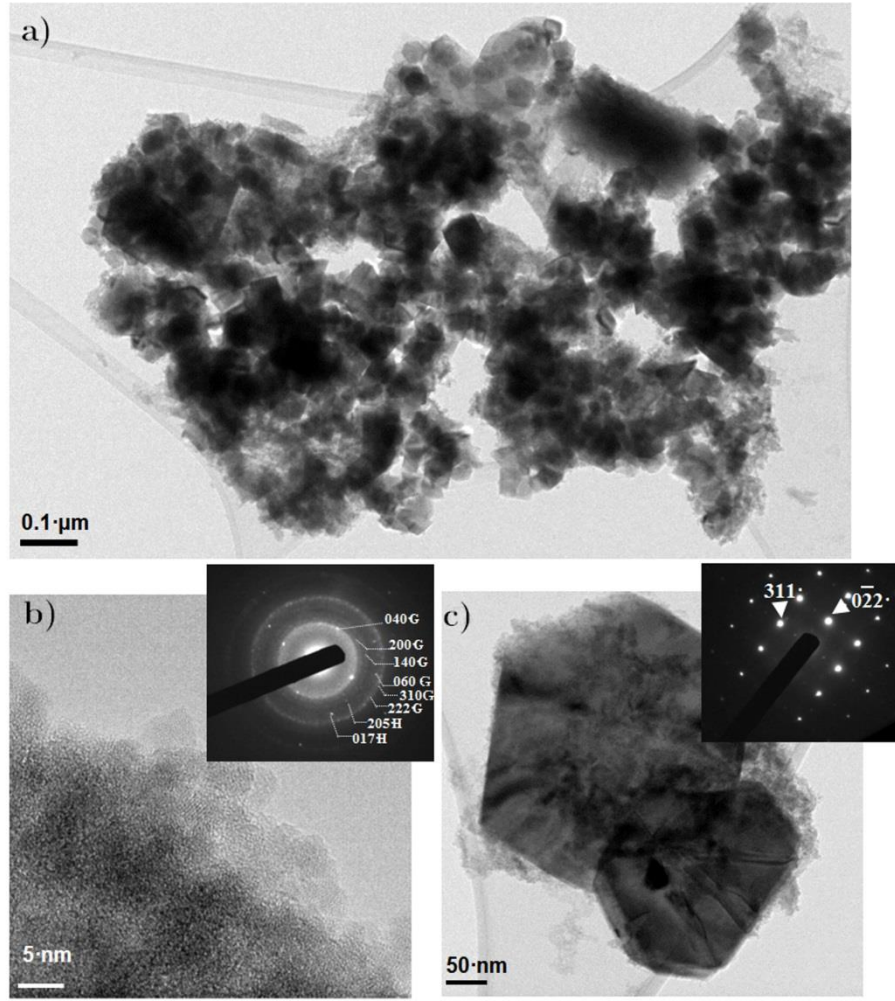


Figure 4.3: Representative TEM images of the MNP-60-10 sample. Figure b) shows smaller spherical nanoparticles (corresponding SAED pattern is indexed according to the structures of goethite (G) and hematite (H)). Figure c) shows larger, octahedrally-shaped particles. The SAED pattern, which was taken at the upper large particle corresponds to the cubic spinel structure along $[233]$.

The sample MNP-60-10 was magnetically characterized using the vibrating sample magnetometer (VSM). The magnetic hysteresis of the sample is presented in Figure 4.4. The M_s of the sample yields $29 \text{ Am}^2/\text{kg}$, which is much too low for the maghemite particles of several tens of nm in size. The well crystalline particles of that size should display M_s close to that of the bulk ($86 \text{ Am}^2/\text{kg}$) [3, 22]. For example, even approximately 10 nm large, superparamagnetic maghemite nanoparticles display $M_s \approx 66 \text{ Am}^2/\text{kg}$ [91]. The low M_s of the sample resulted from the presence of non-magnetic nanoparticles ($\alpha\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$), observed in TEM. The sample MNP-60-10 displayed H_C of 8 kA/m consistent with their relatively large size, much above a superparamagnetic limit.

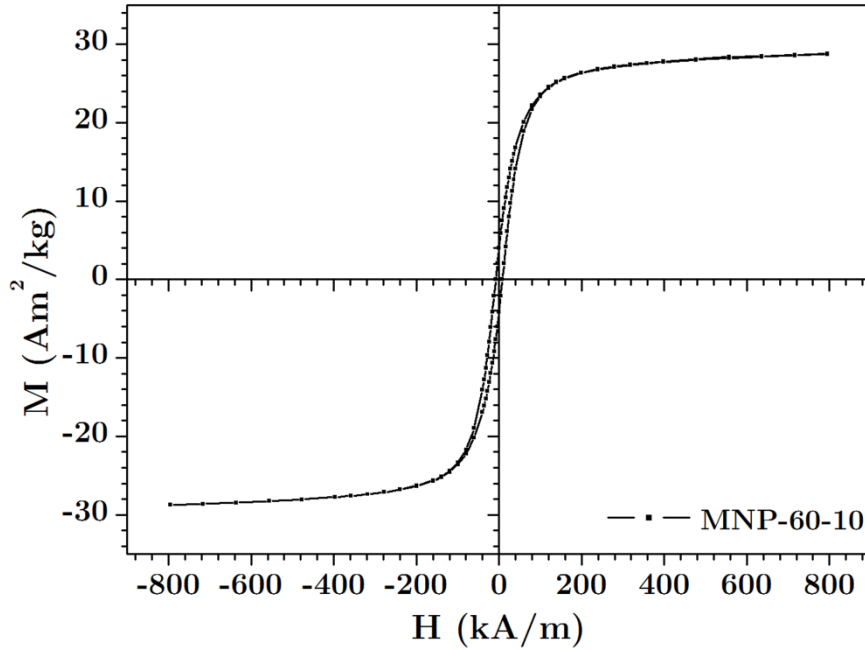


Figure 4.4: Magnetic hystereses of the MNP-60-10 sample.

The sample MNP-60-10 was prepared using the same reaction conditions as were used in the case of the deposition of the spinel-ferrite shell on the core nanoparticles, however without the cores. In the case where hexaferrite core nanoparticles were coated only the maghemite was formed in a form of a layer nucleated on their surface. Other secondary phases could not be observed [72, 76].

However, when the hexaferrite cores were not present, the sample contained beside the spinel-ferrite nanoparticles also the secondary α -Fe₂O₃ and α -FeOOH phases. The spinel-ferrite nanoparticles were well crystalline, over 30 nm in size, suggesting that they were formed at the low supersaturation.

As these secondary phases are non-magnetic, they decrease the magnetization of the sample. The M_s of the sample is therefore a very good measure for the content of the spinel ferrite in the sample. If the ferrite nanoparticles show considerable H_C , their size is above the superparamagnetic limit, which is approximately 20 nm. The spinel-ferrite nanoparticles of the size above 20 nm display M_s above 70 Am²/kg [3, 22].

There are many explanations possible to explain the formation of the secondary phases. My hypothesis is that the formation of the secondary α -Fe₂O₃ and α -FeOOH phases is a consequence of the fast decomposition of the Fe-urea complex. Formation of the secondary phases in the sample suggests growth of the initially formed γ -FeOOH nanoparticles in the first stage of the precipitation process. Formation of different iron-oxide phases depends on the reaction conditions, e.g. reactant concentration, temperature, time. When the reactant concentration is low, the hexaaqua ions ([Fe(H₂O)₆]³⁺) predominantly hydrolyze into lepidocrocite (γ -FeOOH). The γ -FeOOH is a metastable phase, which is stable only in the form of small nanoparticles with a size below 5 nm. With time the γ -FeOOH nanoparticles grow and transform into α -FeOOH nanoparticles. The α -FeOOH phase is more stable when it is present in the form of larger nanoparticles [22, 92]. The rate of γ -FeOOH nanoparticles growth increased with temperature.

The spinel-ferrite could only be formed when the small nanoparticles of γ -FeOOH are present. The size of the nanoparticles depends on the nucleation rate and the growth rate. Both processes depend on the reaction temperature, reaction time and concentration of the released Fe^{3+} ions. Furthermore, the concentrations of released Fe^{3+} ions, which determine the supersaturation, depend on the concentration and decomposition rate of the Fe-urea complex. The decomposition rate of the complex depends on the temperature and pH.

As I mentioned above, the nucleation and growth rates are strongly influenced by the supersaturation of the precipitating species. Moreover, the process of nucleation is influenced also by the presence of the core nanoparticles, especially when the formation of low-energy interfaces is possible.

The results in this section show that a product is different when the core nanoparticles are not present in the reaction mixture. The controlled co-precipitation of the iron ions in the presence of hexaferrite nanoparticles resulted in the single-phase maghemite, whereas without the cores nonmagnetic secondary phases were formed. The formation of non-magnetic phases could indicate that the Fe-urea complex decomposes too fast (i.e. at too low pH). The result of rapid decomposition of the complex is high concentration of Fe^{3+} ions, which are consumed for the growth of the γ -FeOOH.

Therefore, to prevent rapid growth of the γ -FeOOH nanoparticles due to the large concentration of released Fe^{3+} ions, the Fe-urea complex should decompose slower. The concentration of released Fe^{3+} ions depends on the kinetics of the Fe-urea decomposition. The kinetics of the complex decomposition can be influenced by the temperature or pH [76].

4.1.1.1 Influence of reaction temperature on the controlled co-precipitation method

Beside the pH, the decomposition rate of the Fe-urea complex depends also on the temperature. The complex starts to decompose at the temperatures above 45 °C, resulting in a slow and homogeneous release of the Fe^{3+} ions into the solution. With varying the reaction temperature, we could influence the decomposition rate and consequently the concentration of released Fe^{3+} ions. However, the temperature does not only influence the complex decomposition, but also the dissolution of $\text{Mg}(\text{OH})_2$, which influences the pH. The $\text{Mg}(\text{OH})_2$ displays relatively low solubility at room temperature (0.01 g/L), which increases with increasing temperature [93].

To investigate the influence of temperature on the final product of the controlled co-precipitation, the experiments were conducted as in the basic procedure except that the temperature was varied between 50 and 70 °C (Table 4.1).

Table 4.1: Experimental conditions during the controlled co-precipitation procedure and properties of the products.

Code	React. Cond.		Phase comp**		Magnetic properties		
	T (°C)	t_1^{***} (min)	TEM	XRD	M_S (Am ² /kg)	M_R (Am ² /kg)	H_C (kA/m)
MNP 50-10	50	10	S+H+G	S	39.5	5	8
*MNP 60-10	60	10	S+H+G	S	29	4	8
MNP 70-10	70	10	S+H+G	S	18	2	5.3

*Sample prepared with the basic co-precipitation process

**S stands for spinel (γ -Fe₂O₃), H stands for hematite (α -Fe₂O₃) and G stands for goethite (α -FeOOH)

*** t_1 refers to a time at the final temperature when the hydroxide was admixed into the Fe³⁺/Fe²⁺ ions solution

Figure 4.5 shows the increase of the pH with time after the Mg(OH)₂ addition for the samples prepared at different temperatures. The changing of the temperature had only a minor effect on the increase of the pH.

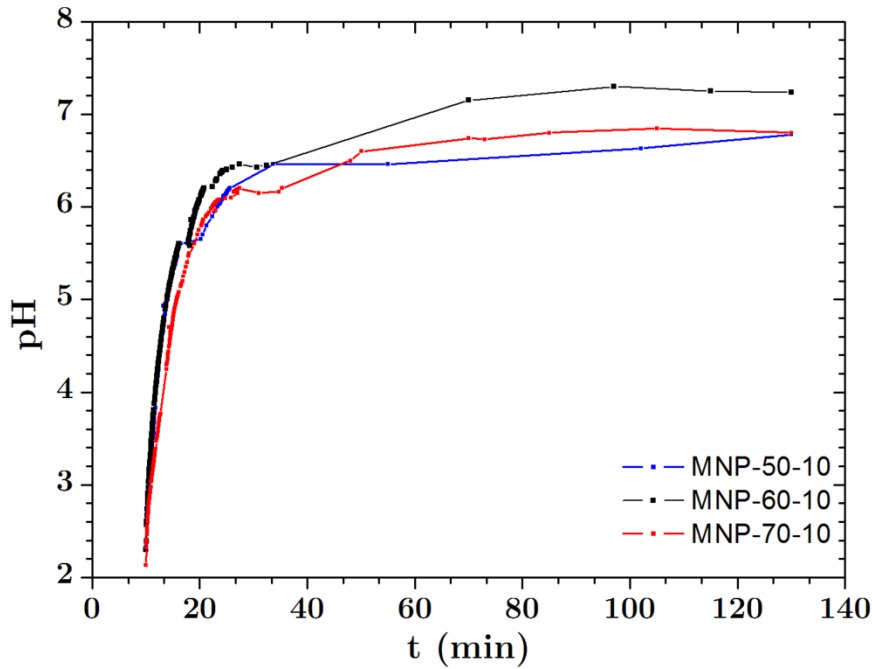


Figure 4.5: Increase of pH with time after Mg(OH)₂ was added in the reaction mixture for three samples prepared at different temperatures.

XRD and TEM analysis showed no differences in the phase composition of the samples prepared at the different temperatures. As the α -FeOOH, α -Fe₂O₃ secondary phases are too poorly crystalline to be detected with XRD, the only reliable method, which can be used to detect the content of the spinel ferrite in the samples, are magnetic measurements. Figure 4.6 shows a comparison between the magnetic hysteresis of the samples, prepared at different temperatures. The comparison revealed that the M_S increases with decreasing reaction temperature. However, the M_S is still significantly lower than the expected values for the well crystalline maghemite nanoparticles with a size above 20 nm.

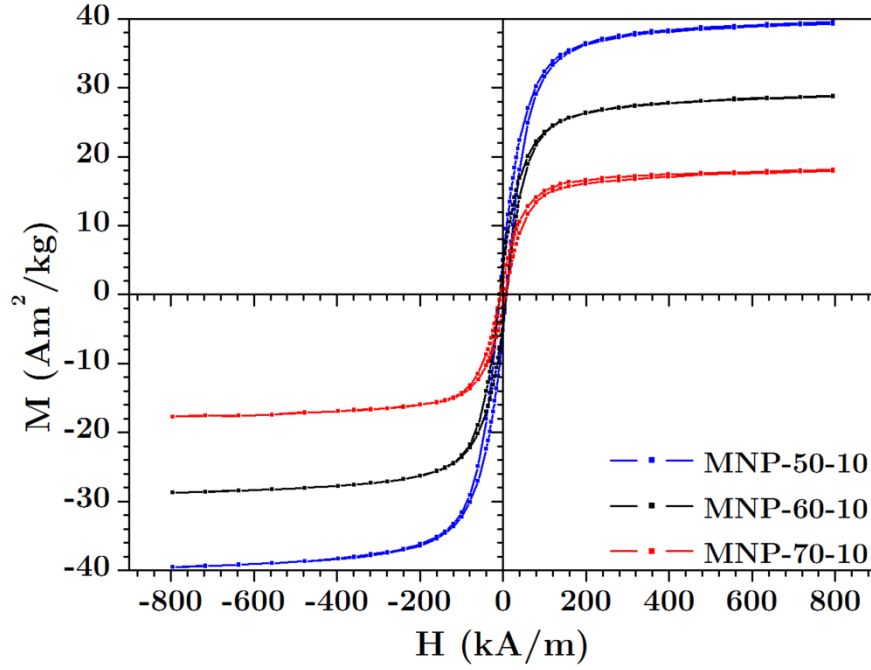


Figure 4.6: Hystereses of samples prepared at different temperatures.

The experiments showed that at the lower temperature the larger content of magnetic spinel ferrite was formed. As hypothesized above, the temperature can influence the decomposition rate of the Fe-urea complex. The decomposition rate determines the concentration of released Fe^{3+} ions in the first stage of the controlled precipitation process. The formation of a larger amount of the spinel ferrite in the lower temperature could be explained according to my hypothesis as follows:

The Fe-urea complex decomposes more slowly at lower temperatures. In the first stage of the controlled precipitation process, slow decomposition of the complex resulted in a slow and homogeneous release of the Fe^{3+} ions into the solution. Slow release of the Fe^{3+} ions resulted in a low concentration of released Fe^{3+} ions and consequently in low supersaturation. Due to low supersaturation, the $\gamma\text{-FeOOH}$ particles grow slowly and a larger amount of them react with precipitating Fe^{2+} ions into the spinel-ferrite after the addition of $\text{Mg}(\text{OH})_2$, before they transform into the $\alpha\text{-FeOOH}$. When the $\text{Mg}(\text{OH})_2$ is added, only a small amount of $\gamma\text{-FeOOH}$ nanoparticles react with Fe^{2+} ions and transform into the spinel ferrite, while larger $\gamma\text{-FeOOH}$ nanoparticles transform into the $\alpha\text{-FeOOH}$ nanoparticles. However, the temperature could not be decreased below 45 °C, since below this temperature, the Fe-urea complex does not decompose at the given pH of 2.2.

Nevertheless, the non-magnetic secondary phases were observed also when the reaction proceeded at 50 °C (Table 4.1). This indicates that the Fe-urea complex still decomposes too quickly, resulting in the growth of the initially formed $\gamma\text{-FeOOH}$ nanoparticles and its transformation into the $\alpha\text{-FeOOH}$. The $\gamma\text{-FeOOH}$ particles grow due to the large concentration of Fe^{3+} ions. Since the reaction temperature could not be further decreased, the concentration of the released Fe^{3+} ions could be controlled also with the duration of incubation time, allowed for the thermal decomposition of the Fe-urea complex during the first stage of the precipitation process.

4.1.1.2 Influence of the duration of the complex decomposition on the controlled co-precipitation process

The formation of the final product is determined by the formation of the initially formed oxide-hydroxide phase. Depending on the reaction conditions: temperature and incubation time, the Fe^{3+} ions could form different iron oxide-hydroxides (γ -FeOOH or α -FeOOH). The transformation between those two FeOOH modifications is influenced by the size of the nanoparticles, which depends on the concentration of Fe^{3+} ions. Only if the FeOOH is in its γ -FeOOH structural modification, it will react with precipitating Fe^{2+} ions to form a magnetic spinel ferrite [76]. In the first stage of the precipitation process the acidic solution containing iron precursors is maintained at an elevated temperature for the incubation time t_1 . In our previous research it was found that optimal t_1 was 10 minutes [76]. During this period of time the complex decomposes and the released Fe^{3+} ions hydrolyze and form γ -FeOOH. With prolonging the t_1 , the γ -FeOOH nanoparticles grow and at a certain size they transform into the α -FeOOH.

Therefore shortening the t_1 will increase the concentration of the Fe^{3+} ions that will precipitate at the higher pH, where the Fe^{2+} ions precipitate. This will prevent the growth of γ -FeOOH and moreover it will enable the simultaneous precipitation of iron ions. In this section I have investigated the effect of the incubation time allowed for the complex thermal decomposition at the acidic conditions on the controlled co-precipitation process.

The experiments were conducted as in the case of the experiments described in the previous section (Section 4.1.1.), except with varying the t_1 between 0 and 10 minutes. Namely, the $\text{Mg}(\text{OH})_2$ was admixed into the solution heated at 50 or 60 °C, together with the reactants ($t_1 = 0$ min), after 5 minutes, or after 10 minutes from the addition of the iron precursors ($t_1 = 5$ min or 10 min) (Table 4.2).

Table 4.2: Experimental conditions during the controlled co-precipitation procedure and properties of the products.

Code	React. Cond.		Phase comp.**		Magnetic properties		
	T (°C)	t_1^{***} (min)	TEM	XRD	M_s (Am ² /kg)	M_R (Am ² /kg)	H_C (kA/m)
MNP 50-0	50	0	S+H+G	S	16.5	2.4	5.5
MNP 50-5	50	5	S+H+G	S	16.5	1.8	7
MNP-50-10	50	10	S+H+G	S	39.5	4	8
MNP 60-0	60	0	S+H+G	S	14.5	1.9	4.5
MNP 60-5	60	5	S+H+G	S	17.5	2	7
*MNP-60-10	60	10	S+H+G	S	29	2	5.3

*Sample prepared with the basic co-precipitation process

**S stands for spinel (γ -Fe₂O₃), H stands for hematite (α -Fe₂O₃) and G stands for goethite (α -FeOOH)

** t_1 refers to a time at the final temperature when the hydroxide was admixed into the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions solution

The XRD and TEM analyses of the samples prepared at different temperatures with varying the t_1 showed no differences compared to the sample MNP-60-10 obtained using the basic procedure. The XRD pattern shows only the peaks that can be indexed according to the cubic spinel structure, whereas the TEM showed secondary phases α -FeOOH and α -Fe₂O₃. The comparison of magnetic properties of the samples prepared at 50 and 60 °C by varying the incubation time is shown in Figure 4.7 a) and b),

respectively. The comparison of the magnetic properties shows that the M_s decreases with decreasing the incubation time.

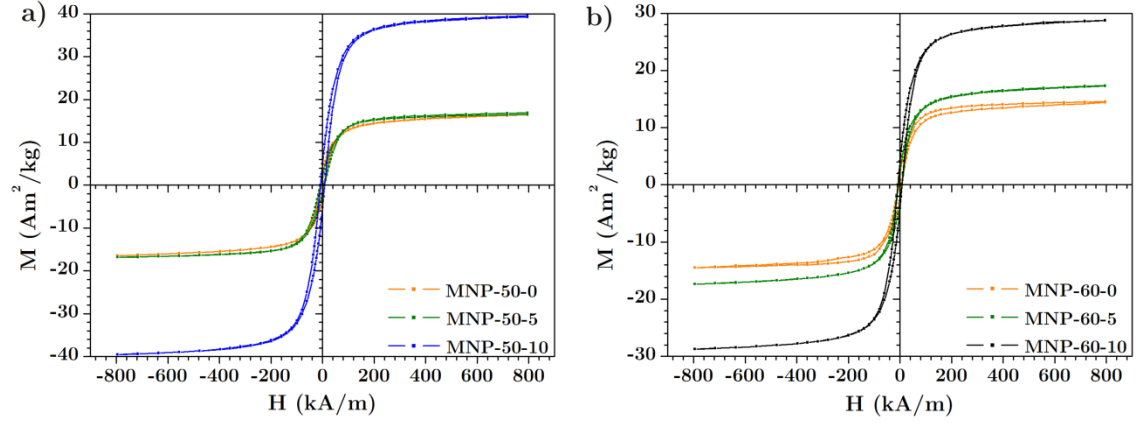


Figure 4.7: Magnetic properties of the samples prepared at 50 °C a) and 60 °C b) with varying the incubation time.

The magnetic measurements showed that much larger fraction of secondary phases were formed, when the t_1 was shortened. This is not in accordance with my assumption that the secondary phases appear as the consequence of the γ -FeOOH-to- α -FeOOH transformation with growth of the γ -FeOOH nanoparticles. The reason for the increase in the content of the secondary phases when the t_1 was decreased is not clear. It would be logic to increase the t_1 , however, our previous research [76] showed that also the prolongation of the t_1 above the optimal 10 minutes results in the appearance of the secondary phases.

4.1.1.3 Influence of the starting pH on the formation of the final product during the co-precipitation procedure

The thermal decomposition of the dissolved Fe-urea complex is influenced by the pH of the solution. In this section I investigated the influence of the starting pH of the solution on the complex decomposition and formation of the final products. I assume that the non-magnetic secondary phases are formed due to the growth of the γ -FeOOH nanoparticles, before they react with Fe^{2+} and transform into the spinel ferrite. To shorten the time between the γ -FeOOH formation and Fe^{2+} precipitation, I increase the starting pH of the suspension containing the iron precursors. The complex decomposition and thermal hydrolysis of the released Fe^{3+} ions is expected to proceed much faster at the higher pH. The ratio between the decomposition rate and the hydrolysis rate determines the concentration of Fe^{3+} ions in the solution.

With adjusting the starting pH on a higher value, the first stage of the controlled co-precipitation process will proceed closer to the pH values where the Fe^{2+} ions precipitate. My hypothesis was as follows: if the formation of initial γ -FeOOH will occur closer to the pH value of the Fe^{2+} precipitation, this could limit its growth and transformation to the non-magnetic α -FeOOH. However, it is expected that the Fe-urea will decompose much faster at the higher pH values when the solution will be heated to the final temperature. Therefore, I assumed that the reactions could proceed also at the lower temperatures where the complex does not decompose at the pH of 2.2.

To evaluate the effect of the starting pH in the controlled co-precipitation process, the reactants were admixed into water and bubbled with argon at room temperature.

Dissolving the complex in water at room temperature resulted in a yellow solution with a pH of 2.4. The starting pH of the solution was adjusted with NaOH to the pH of 4 or 5. The solution remains clear even when the pH was raised above the pH value of 2.8, required for the precipitation of the Fe^{3+} ions. Addition of the NaOH resulted in the change of the solution color to light orange. After the pH adjustment the solution was heated to the chosen temperature (45 or 50 °C). Heating of the solution containing Fe-urea complex and Fe^{2+} ions at the chosen pH resulted in a change of the color from light to dark orange, however the solution remained clear, proving that no precipitation occurred. The change of the color occurs when the temperature approaches 45°C. The color change indicates that the Fe^{3+} ions were released from the complex and present in the solution in the form of hexaaqua ions ($[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$) [22]. The solid $\text{Mg}(\text{OH})_2$ was admixed immediately after the solution reached the chosen temperature ($t_l = 0$ min) or with delay of 10 minutes ($t_l = 10$ min) (Table 4.3.). The addition of the solid hydroxide resulted in a rapid increase of the pH resulting in the change of the color from orange to dark brown and after approximately 30 minutes to black. In all experiments listed in Table 4.3 the pH value of 5.6, where Fe^{2+} ions start to precipitate, was reached within approximately 1 minute after the addition of the hydroxide.

Table 4.3: Experimental conditions during the controlled co-precipitation procedure and properties of the products.

<i>Code</i>	<i>React. Cond.</i>			<i>Phase comp.*</i>		<i>Magnetic properties</i>		
	<i>T</i> (°C)	<i>t_l**</i> (min)	<i>pH</i>	<i>TEM</i>	<i>XRD</i>	<i>M_S</i> (Am ² /kg)	<i>M_R</i> (Am ² /kg)	<i>H_C</i> (kA/m)
<i>RT4-50-10</i>	50	10	4	S+H+G	S	15	2.5	1.4
<i>RT5-50-10</i>	50	10	5	S+H+G	S	10	4.7	1.3
<i>RT4-50-0</i>	50	0	4	S+H+G	S	25	5.7	3.7
<i>RT5-50-0</i>	50	0	5	S+H+G	S	13	5	1.8
<i>RT4-45-10</i>	45	10	4	S+H+G	S	28	5	7
<i>RT5-45-10</i>	45	10	5	S+H+G	S	24	3.5	5.2
<i>RT4-45-0</i>	45	0	4	S+H+G	S	12	1.5	5.2
<i>RT5-45-0</i>	45	0	5	S+H+G	S	25	3	5

*S stands for spinel (γ - Fe_2O_3), H stands for hematite (α - Fe_2O_3) and G stands for goethite (α - FeOOH).

** t_l refers to a time at the final temperature when the hydroxide was admixed into the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions solution

The XRD and TEM analyses of the samples listed in Table 4.4 showed no differences in the phase composition compared to the sample MNP-60-10 obtained using the basic process. Therefore, as in the previous cases, the only reliable analysis to reveal the content of the magnetic spinel-ferrite phase in the sample remained the magnetic measurements. Figure 4.8 a) and b) represent the comparison of the magnetic properties of the samples prepared at 45 and 50 °C, respectively. The comparison of the magnetic properties shows that the M_S decreases with increasing starting pH, except for the samples prepared at 45 °C where $t_l = 0$. Here the M_S increases with the increase of the starting pH.

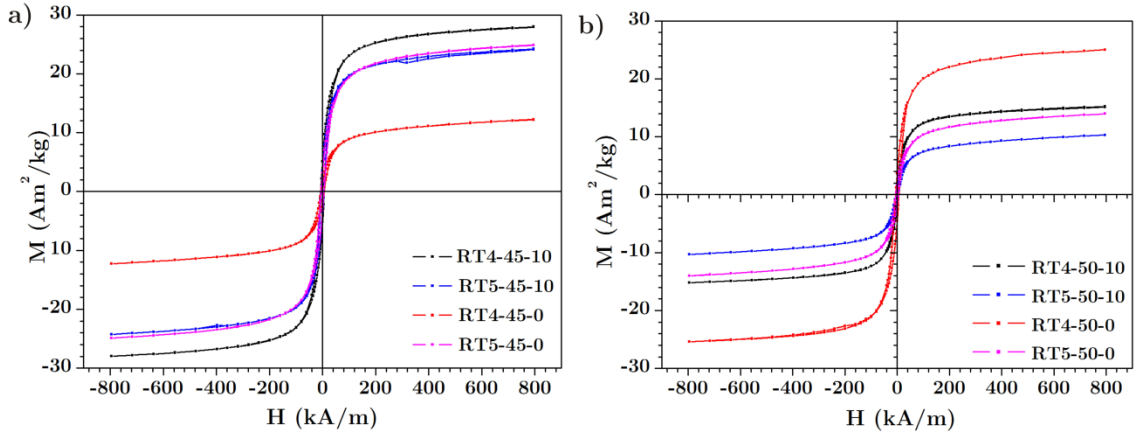


Figure 4.8: Magnetic properties of samples prepared at 45 °C a) and 50 °C b) with varying the starting pH of the suspension incubation time.

Among the samples, where the formation of initial γ -FeOOH occurs in acidic media, the largest M_s was observed for the sample MNP-50-10 ($M_s = 39.5 \text{ Am}^2/\text{kg}$) (see Figure 4.7). The magnetic measurements of the samples prepared with adjusting the starting pH to the higher values showed the increased amount of secondary phases, compared to the sample MNP-50-10.

The results are not in accordance with my hypothesis that the growth of the initially formed γ -FeOOH will be limited if its formation will occur closer to the pH of 5.6, where the Fe^{2+} ions start to precipitate. Due to the complex mechanism, there is no simple explanation for the increased amount of non-magnetic phases. A possible explanation can be related to partial oxidation of the Fe^{2+} ions into the Fe^{3+} during the heating of the solution to the final temperature. Even though the solution is bubbled with argon; there could still be a small concentration of dissolved oxygen, which resulted in an oxidation of Fe^{2+} ions. To prevent the oxidation and, at the same time, to establish the conditions favoring formation of the spinel ferrite (magnetite) over the formation of the hematite, slightly reductive conditions were used in the next experiments, described in the next chapter.

4.1.1.4 Influence of the starting pH on the formation of the final product during the co-precipitation procedure under reductive conditions

The deposition of spinel-ferrite layers onto the surface of the core nanoparticles proceeds under inert conditions. Namely, suspension of core nanoparticles containing the Fe-urea complex and Fe^{2+} ions is bubbled with argon to expel dissolved oxygen. However, some of the dissolved oxygen can remain in the solution. Moreover, in the reaction mixture some mild oxidizing agents, e.g. nitrate ions, are present, which can cause partial oxidation of the Fe^{2+} before they precipitate and react with the γ -FeOOH into the spinel. This will result in a shortage of Fe^{2+} ions needed for transformation of γ -FeOOH to the spinel-ferrite. As explained above, any γ -FeOOH that will not react with Fe^{2+} ions will transform into the non-magnetic α -FeOOH.

I assumed that the larger amount of the secondary phases in the samples presented in the previous section resulted from the partial oxidation of Fe^{2+} ions during the heating step at the increased pH. Therefore this resulted in an increased amount of the non-magnetic secondary phases compared to the sample prepared with the basic procedure.

To prevent the oxidation of Fe^{2+} a reducing agent hydrazine (N_2H_4) was dissolved in the reaction solution. The presence of the reducing agent will also favour the formation of spinel ferrite (magnetite). It is known that the formation of maghemite is thermodynamically favoured over the formation of hematite under the reductive conditions [94].

The experiments described in this section were performed under equal experimental conditions as presented in the previous Section 1.1.1.3, except the addition of hydrazine (Table 4.4.).

Table 4.4: Experimental conditions during the controlled co-precipitation under reductive conditions and properties of the products.

<i>Code</i>	<i>React. Cond.</i>			<i>Phase comp.*</i>		<i>Magnetic properties</i>		
	<i>T</i> (°C)	<i>t₁**</i> (min)	<i>pH</i>	<i>TEM</i>	<i>XRD</i>	<i>M_S</i> (Am ² /kg)	<i>M_R</i> (Am ² /kg)	<i>H_C</i> (kA/m)
<i>RTH4-50-10</i>	50	10	4	S+H+G	S	52	9.5	7
<i>RTH5-50-10</i>	50	10	5	S+H+G	S	43	5	4
<i>RTH4-50-0</i>	50	0	4	S+H+G	S	38	6	5
<i>RTH5-50-0</i>	50	0	5	S+H+G	S	45	6	3
<i>RTH4-45-10</i>	45	10	4	S+H+G	S	26	2.6	2.7
<i>RTH5-45-10</i>	45	10	5	S+H+G	S	31	4.5	4
<i>RTH4-45-0</i>	45	0	4	S+H+G	S	36	5	4.5
<i>RTH5-45-0</i>	45	0	5	S	S	52	7	4

*S stands for spinel ($\gamma\text{-Fe}_2\text{O}_3$), H stands for hematite ($\alpha\text{-Fe}_2\text{O}_3$) and G stands for goethite ($\alpha\text{-FeOOH}$).

** t_1 refers to a time at the final temperature when the hydroxide was admixed into the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions solution

The XRD and TEM analyses of the samples listed in Table 4.4 show no differences compared to the samples prepared without the hydrazine addition, except in the case of the sample RTH5-45-0. A detailed TEM analysis revealed that the secondary phases were absent in the sample RTH5-45-0. The sample contained only 20-100 nm large, globular nanoparticles (Figure 4.9.). The SAED recorded on the large agglomerate shows only the reflection corresponding to the cubic spinel structure (Figure 4.9 b)).

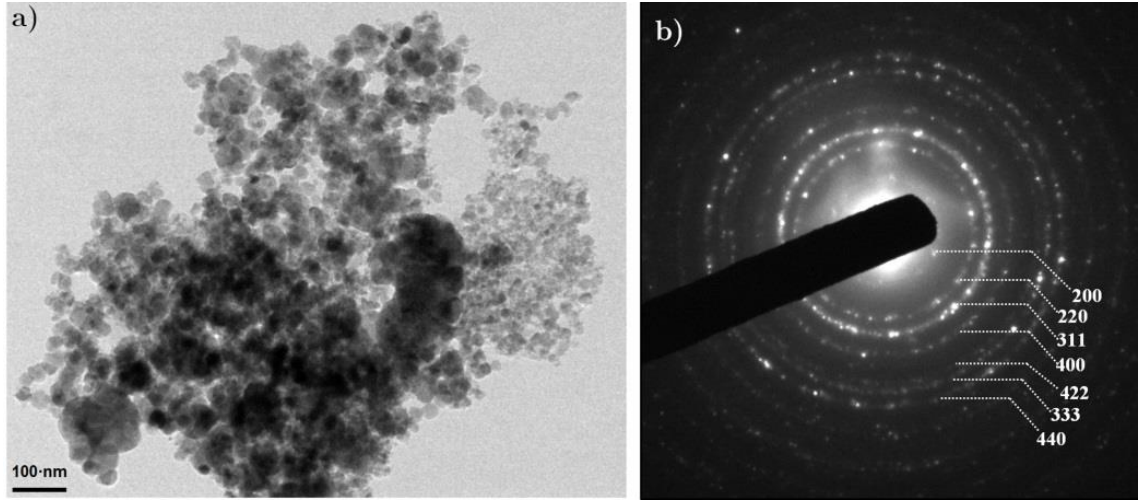


Figure 4.9: Representative TEM image a) of the RTH5-45-0 sample with b) corresponding SAED. The SAED is indexed according to the cubic spinel structure. The sample was prepared under the reductive conditions at 45 °C, where the initial pH was set to 5 and with $t_1 = 0$ min.

Figure 4.10 a) and b) shows a comparison between magnetic properties of the samples prepared under reductive conditions at 45 and 50 °C, respectively. The magnetic measurements showed that the M_s increases with increasing starting pH, except for the sample prepared at 50 °C with t_i of 10 min. Moreover, the samples prepared under reduction conditions display higher M_s values compared to the samples prepared without the hydrazine addition.

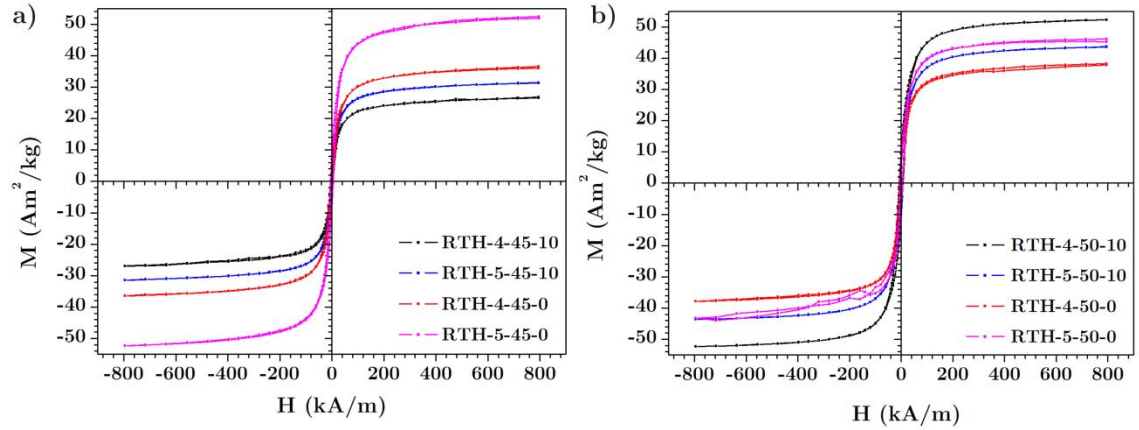


Figure 4.10: Magnetic properties of samples prepared under reductive conditions at 45 °C a) and 50 °C b) with varying the starting pH of the suspension and incubation time.

The magnetic measurements of the samples prepared under reductive conditions showed increased content of the magnetic phase compared to the samples where hydrazine was not added. The results confirm my assumptions that the large amount of the secondary phases resulted from the oxidation of Fe^{2+} ions, and/or the spinel ferrite is favored under the reducing conditions.

For the RTH5-45-0 sample no secondary phases could be detected using TEM analysis. The spinel-ferrite nanoparticles displayed a broad size distribution. The shape of

the nanoparticles was globular – even the largest nanoparticles did not display octahedral shape typical for well-crystalline spinel-ferrite nanoparticles. The broad size distribution and the relatively poor crystallinity of the nanoparticles suggest that they were formed under a large supersaturation. This can be an obstacle when the same experimental conditions will be applied for deposition of the spinel-ferrite shells onto the core nanoparticles. The sample RTH5-45-0 displayed large M_s of 52 Am²/kg. The measured M_s is still lower than expected for the spinel-ferrite nanoparticles of their size, suggesting that the secondary phases were formed; however, their content was small. Also the sample RTH4-50-10 showed large M_s of 52 Am²/kg even some particles of secondary non-magnetic phases were observed by TEM. The RTH4-50-10 sample displayed larger H_c compared to the sample RTH4-50-10, indicating the presence of larger magnetic nanoparticles.

4.1.1.4.1 Controlled release of hydroxyl ions

The product prepared under the reductive conditions at 45 °C, with the starting pH of 5, and the $t_i = 0$, contained almost only the spinel-ferrite nanoparticles. I assumed that the spinel-ferrite was formed under a high supersaturation resulting in a rapid burst of nucleation through the reaction vessel. Under such conditions the process is very rapid and it is difficult to be controlled. At such reaction conditions, the controlled heterogeneous nucleation of precipitating species and thus deposition of the spinel-ferrite shell on core nanoparticles is not likely to be possible. In the basic procedure (sample MNP-60-10), low supersaturation of the precipitating species was maintained with controlled release of the Fe³⁺ ions from the complex and with slow and homogeneous release of the OH⁻ ions from the solid hydroxide. However, the same amount of added hydroxide in the case of sample RTH5-45-0 as used in the basic procedure resulted in a rapid increase of the pH (Figure 4.11). The gradual increase and homogeneous release of the OH⁻ ions could be enabled with optimizing the amount of the hydroxide. A smaller amount of the hydroxide would lead to lower concentration of dissolved hydroxyl ions resulting in the lower nucleation rate. If the core nanoparticles are present, such conditions will lead to the heterogeneous nucleation of the product on their surfaces.

The experiments proceeded under the same reaction conditions as in the case of the sample RTH5-45-0, except that the amount of added Mg(OH)₂ was gradually decreased, from 0.32 mmol (used for the sample RTH5-45-0) to 0.08 mmol (Table 4.5).

Figure 4.11 shows changing of the pH with time for the samples synthesized under reductive conditions at 45 °C with initial pH of 5, $t_i = 0$ min, and with a different concentration of the added hydroxide. The initial slope of the pH vs. time curve decreased with the decrease in the amount of hydroxide. However, the time needed for the increase of the pH to the value of the Fe²⁺ precipitation was still within one minute after the addition of the hydroxide.

Table 4.5: Experimental conditions during the controlled co-precipitation under reductive conditions and properties of the products.

<i>Code</i>	<i>React. Cond.</i>			<i>Phase comp.*</i>		<i>Magnetic properties</i>		
	<i>T</i> (°C)	<i>t₁**</i> (min)	<i>pH</i>	<i>TEM</i>	<i>XRD</i>	<i>M_S</i> (Am ² /kg)	<i>M_R</i> (Am ² /kg)	<i>H_C</i> (kA/m)
<i>RTH5-45-0</i>	45	0	5	S	S	52	7	4
RTH5-45-0M ₁₆	45	0	5	S+H+G	S	46	8.7	8
RTH5-45-0M ₈	45	0	5	S+H	/	2.8	0	0

*S stands for spinel (γ -Fe₂O₃), H stands for hematite (α -Fe₂O₃) and G stands for goethite (α -FeOOH).

** *t₁* refers to a time at the final temperature when the hydroxide was admixed into the Fe³⁺/Fe²⁺ ions solution

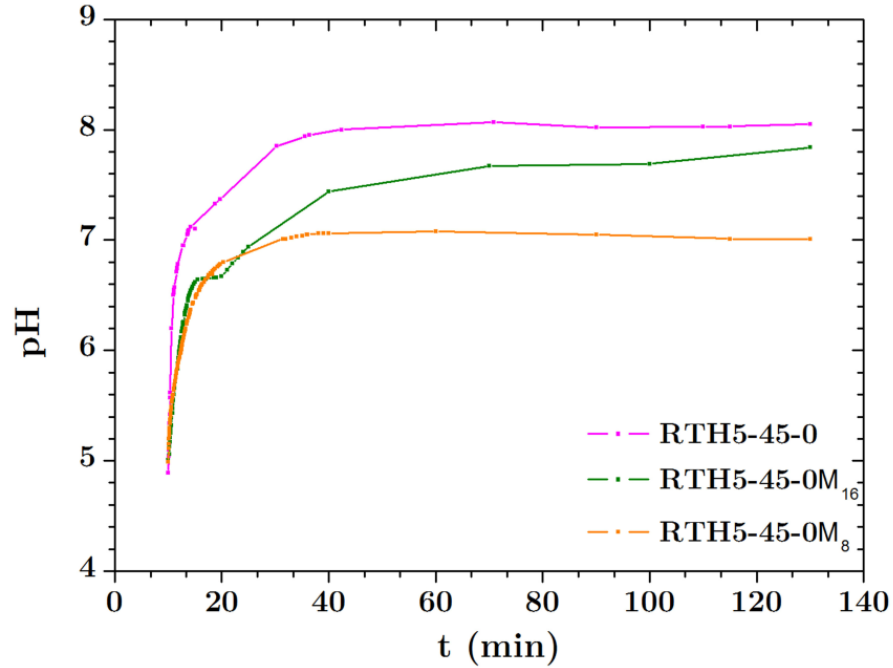


Figure 4.11: pH vs. time curve for RTH5-45-0, RTH5-45-0M₈ and RTH5-45-0M₁₆ samples.

XRD analysis of the RTH5-45-0M₁₆ sample showed only peaks of the spinel, the same as the RTH5-45-0 sample, whereas the RTH5-45-0M₈ sample was not crystalline enough to form any peaks above the background signal. TEM analysis of the RTH5-45-0M₈ sample showed only 5-10 nm large nanoparticles (Figure 4.12). The corresponding SAED showed only weak reflections that can be indexed according to the α -FeOOH and α -Fe₂O₃ (Figure 4.12 c)).

The TEM analysis of the sample RTH5-45-0M₁₆ showed the spinel-ferrite nanoparticles as the major phase and low content of the secondary α -FeOOH and α -Fe₂O₃ phases.

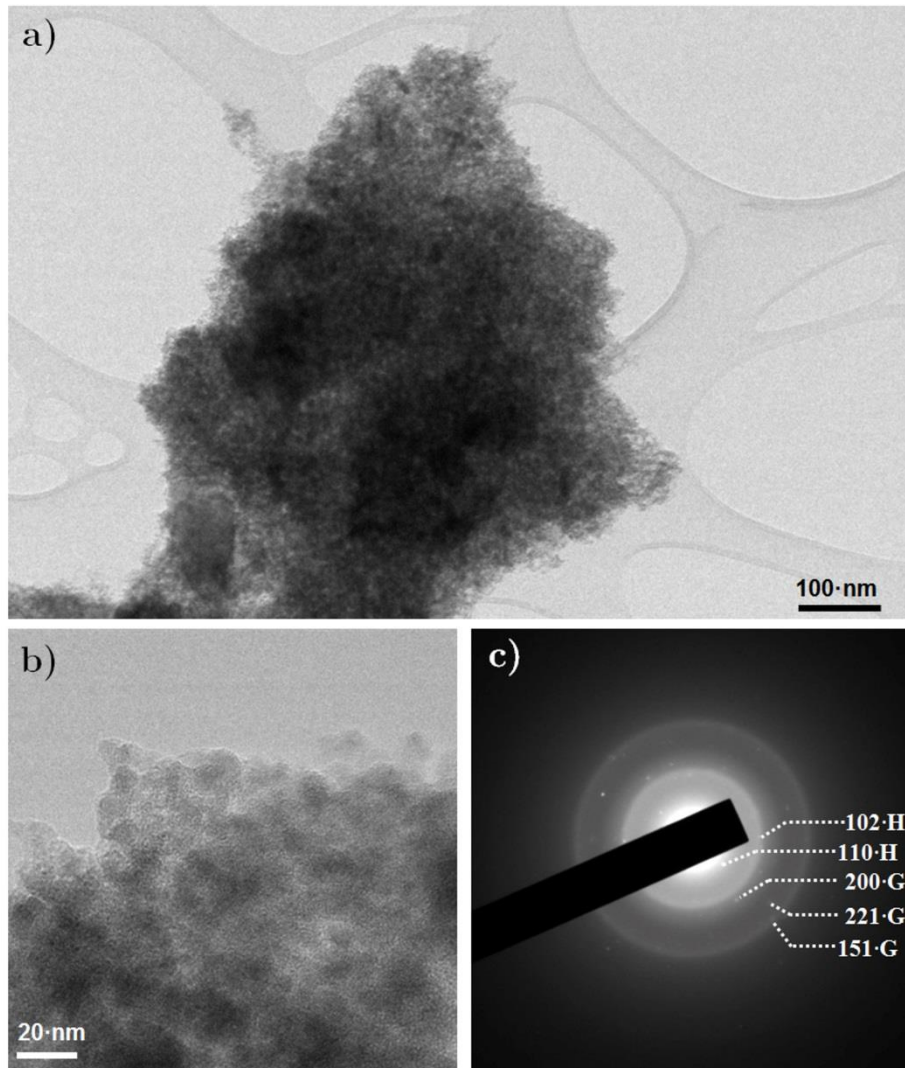


Figure 4.12: Representative TEM images of the RTH5-45-0M₈ sample. Figure b) shows smaller spherical nanoparticles and c) corresponding SAED pattern which could be indexed according to the structures of goethite (G) and hematite (H).

Figure 4.13 shows magnetic properties of the samples prepared with different amounts of the Mg(OH)₂. The magnetic measurements revealed that M_s decrease with the decreasing amount of the added hydroxide (Table. 4.5.). The M_s of the sample RTH5-45-0M₈ was only 2.5 Am²/kg in accordance with the presence of non-magnetic α -FeOOH and α -Fe₂O₃. With addition of 0.08 mmol of the Mg(OH)₂ the final pH was too low for the transformation of the γ -FeOOH to the spinel ferrite.

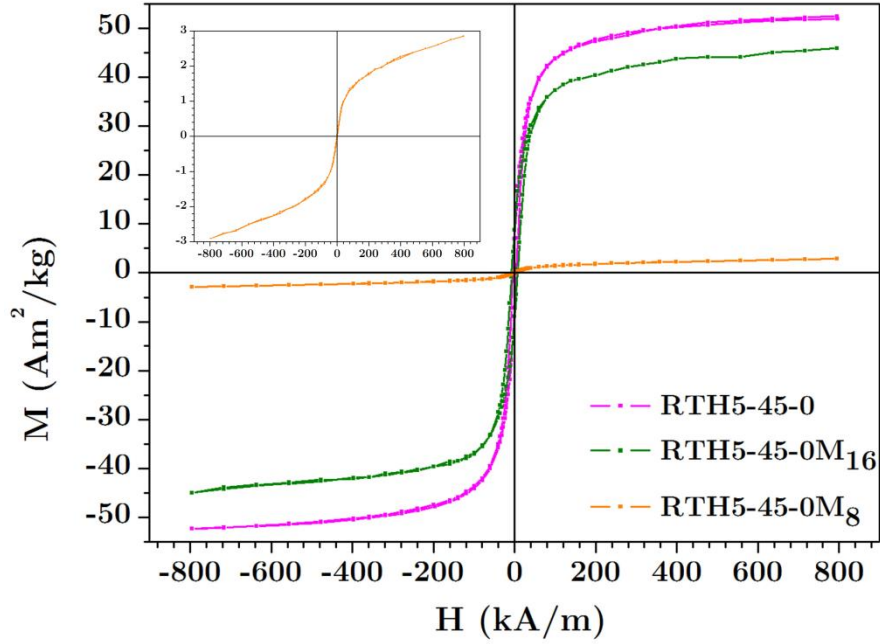


Figure 4.13: Magnetic properties of samples RTH5-45-0, RTH5-45-0M₈ and RTH5-45-0M₁₆.

4.1.2 Discussion of synthesis of the magnetic spinel iron oxide nanoparticles with controlled co-precipitation

Section 4.1 shows the systematic investigation of the controlled co-precipitation method. In the presence of the hexaferrite core nanoparticles the controlled co-precipitation results in single-phase maghemite, which heterogeneously nucleates on the surfaces of the core nanoparticles to form the shell [72]. When some other nanoparticles were used as the cores, the spinel-ferrite shell was not formed. Also, the investigation of the controlled co-precipitation without the core nanoparticles showed that under the applied conditions some unwanted non-magnetic α -FeOOH and α -Fe₂O₃ secondary phases were formed. I focused on the reaction parameters, which could enable conditions for a successful deposition of a spinel-ferrite shell onto core nanoparticles in the aqueous suspension. The research showed that the formation of spinel ferrite was favored under reducing conditions, at lower temperature, and at increased starting pH. Almost single-phase spinel ferrite was obtained, when the hydrazine was added, the initial pH of the solution was adjusted to 5 and Mg(OH)₂ was added immediately after the temperature reached 45 °C (sample RTH5-45-0). However, the co-precipitation proceeded under high supersaturation. The high supersaturation could be the problem in application of these experimental conditions for deposition of the magnetic shells onto the core nanoparticles. In order to achieve low supersaturation which promotes heterogeneous nucleation, the concentration of the added hydroxide was decreased. However, when the hydroxide was decreased the content of the unwanted non-magnetic secondary α phases increased because of the low final pH.

4.2 Composite Nanoparticles

4.2.1 Bi-magnetic nanoplatelets (CNP)

The following section presents bi-magnetic composite nanoplatelets synthesized by deposition of maghemite layers of different thickness onto barium-hexaferrite (later referred to as HF) core nanoplatelets. The maghemite layers were deposited to engineer magnetic properties of the nanoplatelets.

The barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) is a hard-magnetic material. It crystalizes in a magnetoplumbite structure which can be presented as a closed-packed arrangement of larger Ba and O atoms with smaller Fe atoms at the interstitials. The structure can be divided into two alternating structural blocks: the hexagonal “R” block and the cubic “S” block stacked along the c-direction. The growth of the HF crystals is limited in the c-direction and therefore they grow in the form of hexagonal platelets. The most distinguished magnetic property of the HF is a large uniaxial magneto crystalline anisotropy ($K_i=3.3 \times 10^4 \text{ J/m}^3$ in the bulk), which results from its anisotropic crystal structure. The direction of easy magnetization (easy axis) is aligned parallel with the crystallographic c-axis, that is perpendicular to the platelet particles [3]. When the platelet particles are subjected to a magnetic field ($\mathbf{H}$) the direction of its magnetic moment ($\mathbf{m}$) will align with the field resulting in a driving torque ($\boldsymbol{\tau}_m = \mathbf{m} \times \mathbf{H}$) that can be transferred to the surrounding. Due to the high magnetocrystalline anisotropy, the energy needed for rotation of the whole platelet to align with an external magnetic field is lower than the one needed for rotation of the magnetic moment inside the platelet.

The possibility to align the HF crystals magnetically is especially important for some novel applications of the HF nanoparticles. The alignment of the nanoplatelets in a preferential direction can be used for the preparation of magnetically orientated thick films and perpendicular recording media [24]. Moreover, the effect can make the foundation for new magnetically responsive materials, such as magneto-optic composites [95], soft magneto-electrics [96-98] and magneto-viscous fluids [98, 99]. Magneto-mechanical actuation of the nanoplatelets in a low frequency alternating magnetic field can be applied for remote control of nanomedicines and drug delivery systems [100-102]. The effective coupling of the nanoparticles' magnetic moments with a magnetic field can also be used in sensors of the field direction [103].

Generally, the effect of the magnetic field on the nanoplatelet, e.g., a driving torque, is proportional to the nanoplatelet's magnetic moment, i.e., the product of its volume (V) and saturation magnetization (M_s) ($m = V \cdot M_s$). Usually the size of the nanoparticles is required to remain small by demands of their application. Therefore, to maximize the effect of the field on the nanoplatelet, the M_s should be increased.

As the hard-magnetic material, the HF displays rather modest M_s ($72 \text{ Am}^2/\text{kg}$ in a bulk), whereas in the form of the nanoplatelets the M_s is significantly smaller [85, 86, 104, 105].

The approximately 50 nm wide and 3 nm thick hexagonal nanoplatelets of undoped HF displayed M_s around $20 \text{ Am}^2/\text{kg}$. The relatively low M_s was ascribed to a poor structural order related to the small thickness of the nanoplatelets, which is less than 2 dimensions of the unit cell in the corresponding c-direction of their structure [3]. Doping the HF with Sc enabled significant improvement in the M_s without an increase in their size [85]. The unique properties, i.e., relative high M_s above $30 \text{ Am}^2/\text{kg}$, the anisotropic shape, and the uniaxial magnetic anisotropy enable the use of $\text{BaFe}_{10.7}\text{Sc}_{1.3}\text{O}_{19}$ (BSHF) nanoplatelets for the preparation of some new materials [95, 97-99]. For example, the first ferromagnetic liquids were prepared by dispersing the BSHF nanoplatelets into liquid

crystal [97]. Incorporation of the BSHF nanoplatelets in a transparent polymer matrix was used for the preparation of magneto-optical composites [95]. The mentioned applications are very encouraging, however, they also revealed that for further development the M_s of the nanoplatelets has to be further improved.

The M_s of the hard-magnetic BSHF core nanoplatelets could be significantly improved with coating with soft-magnetic shell [72, 85, 86, 104, 105]. Magnetic iron oxides with spinel structure (Fe_3O_4 – magnetite and $\gamma\text{-Fe}_2\text{O}_3$ – maghemite) are soft-magnetic materials with a relatively high M_s (86 Am²/kg for maghemite), but low, cubic magneto-crystalline anisotropy. It was shown that the coating of the HF with a thin maghemite layer results in an impressive improvement of their M_s without a large increase in their size and the loss of the desired out-of-plane anisotropy [72]. If the two phases are magnetically coupled the formed composite will homogeneously magnetize as a single-phase nanoparticle.

Frequently, material properties, e.g., a shape of hysteresis loop, have to be closely tuned to meet demands of a specific application. Compared to the single-phase nanoparticles, the composites allow much closer control over the properties, since the size of the core and thickness of the shell can be controlled separately. The M_s of the hard/soft magnetic nanoparticles can be maximized by the increase of the thickness of the soft-magnetic shell. However, for effective coupling between the two magnetically different phases, the soft-magnetic shell should remain thin, less than twice the domain-wall width of the hard phase [19, 106].

To increase the M_s and to tune the magnetic properties of the BSHF core nanoplatelets, they were coated with a soft-magnetic maghemite layer of different thicknesses. The maghemite layers were deposited onto the BSHF nanoplatelets using the controlled co-precipitation procedure (see Section 4.1).

4.2.1.1 Properties of hexaferrite core nanoplatelets

BSHF core nanoplatelets with nominal composition $\text{BaFe}_{10.5}\text{Sc}_{1.5}\text{O}_{19}$ were prepared using hydrothermal synthesis at a temperature of 240 °C [85, 86, 104, 105]. Figure 4.14 a) shows a representative TEM image of the BSHF core nanoparticles revealing its platelet morphology. According to measurements from the TEM images the nanoplatelets were 20 to 80 nm wide and ≈ 3 nm thick (Figure 4.14 b)). Figures 4.14 c)-e) show HRTEM and HAADF-STEM images of the BSHF nanoplatelets orientated with basal surfaces parallel to the electron beam.

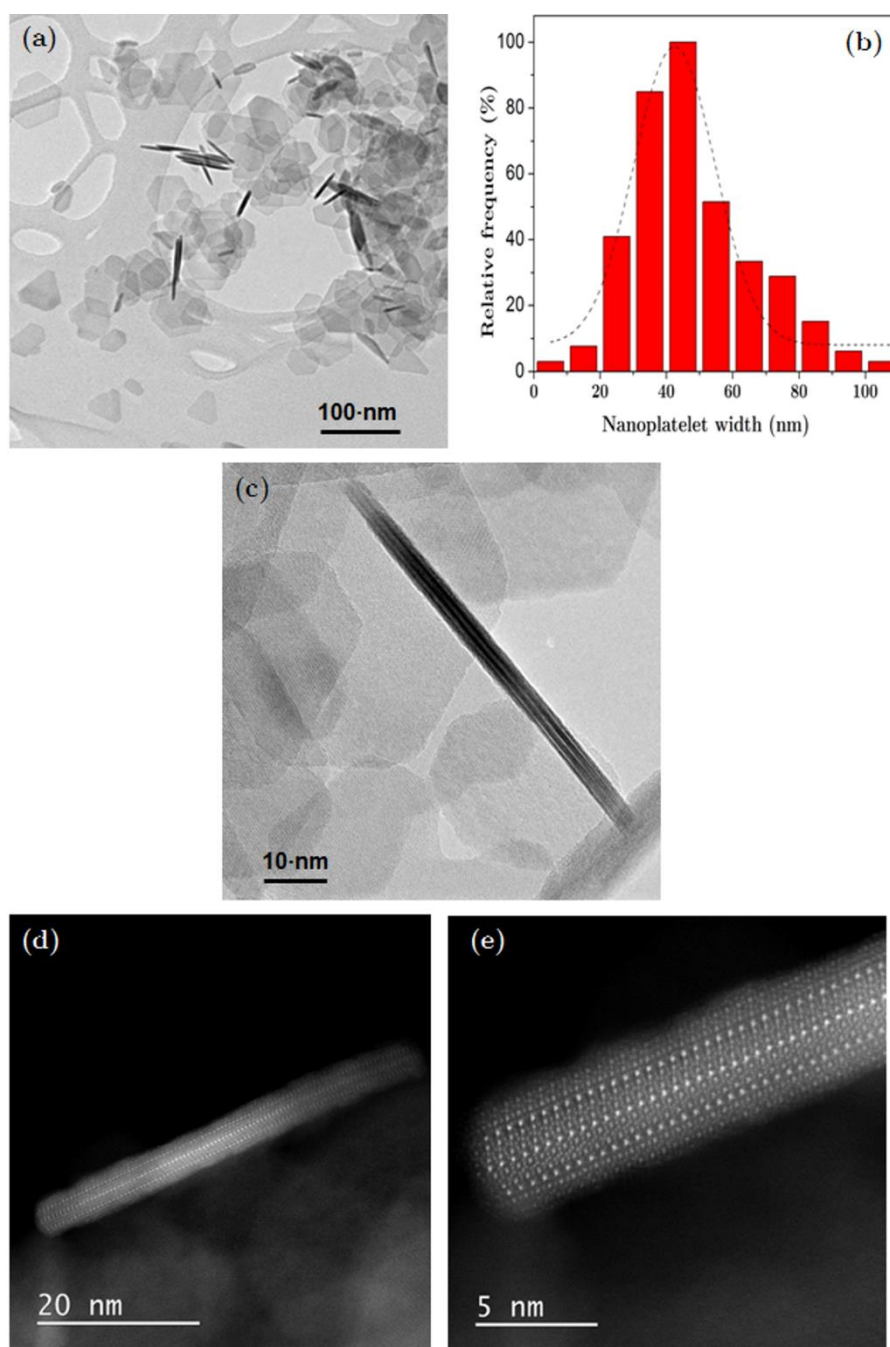


Figure 4.14: BSHF core nanoparticles: a) representative TEM image, b) nanoparticle's width measured from TEM images expressed as an equivalent diameter, c) HREM image, d) and e) HAADF-STEM image of core nanoparticle orientated with the large surface parallel to the electron beam.

Figure 4.15 a) shows an XRD pattern of the BSHF core nanoparticles. The positions of all the peaks correspond to the hexaferrite structure. However, the relative intensities of the peaks differ significantly from those of the bulk (PDF card No. 84-0757). The peaks originating from the (hkl) lattice planes that contain the non-zero l-component are very broad or they are even missing for low l values, due to the very small dimension of the

crystal along the c-direction of the structure, which corresponds to the thickness of the crystal. The nanoparticles' thickness is only approximately 3 nm, which is less than two dimensions of the hexagonal cell along the corresponding c-direction ($a = 0.5892$ nm, $c = 2.318$ nm).

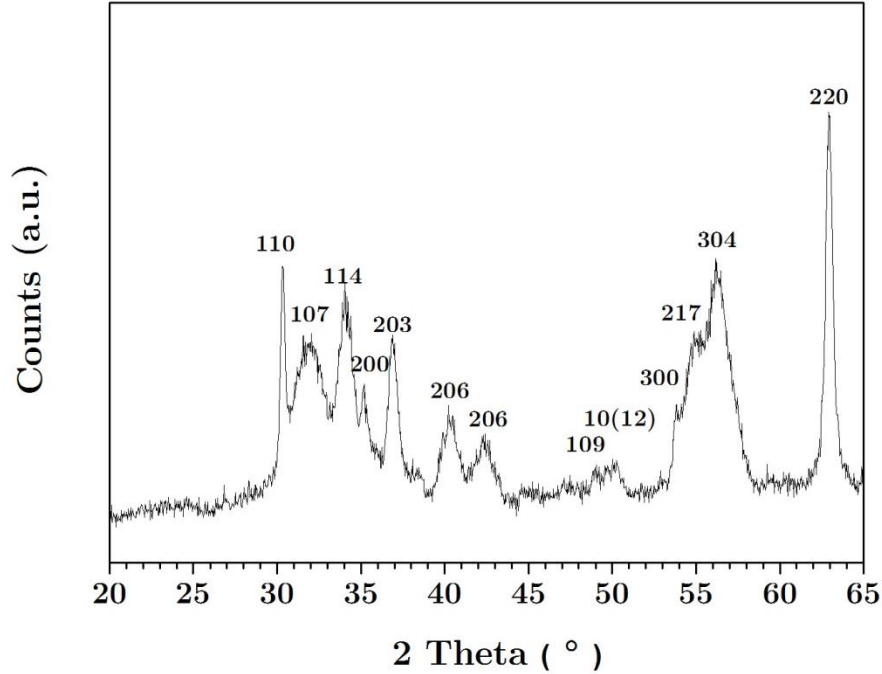


Figure 4.15: XRD pattern of the BSHF nanoplatelets.

The magnetic properties of nanoplatelets powder were measured at room temperature using a vibrating sample magnetometer (Figure 4.16 a)). The M_s of the BSHF nanoplatelets yields around $31 \text{ Am}^2/\text{kg}$, while $M_R \approx 16 \text{ Am}^2/\text{kg}$ and $H_C \approx 80 \text{ kA/m}$. The shape of the hysteresis of the nanoplatelets strongly depends on their orientation. This is illustrated in Figure 4.16 b) where the nanoplatelets were oriented and measured parallel and perpendicular to the c-axis of the nanoplatelets. Prior to the magnetic measurement, the BSHF nanoplatelets were hydrophobized with recinoleic acid and then the low concentration of the nanoplatelets was homogeneously dispersed in a liquid wax. The nanoplatelets were magnetically orientated in the homogeneous magnetic field of 1 T and then the wax was solidified by cooling. The hysteresis of the nanoplatelets measured in parallel (PAR) to the c-direction is much broader than perpendicular (PER) to the c-axis of the BSHF structure in agreement with the expected orientation of the easy-axis.

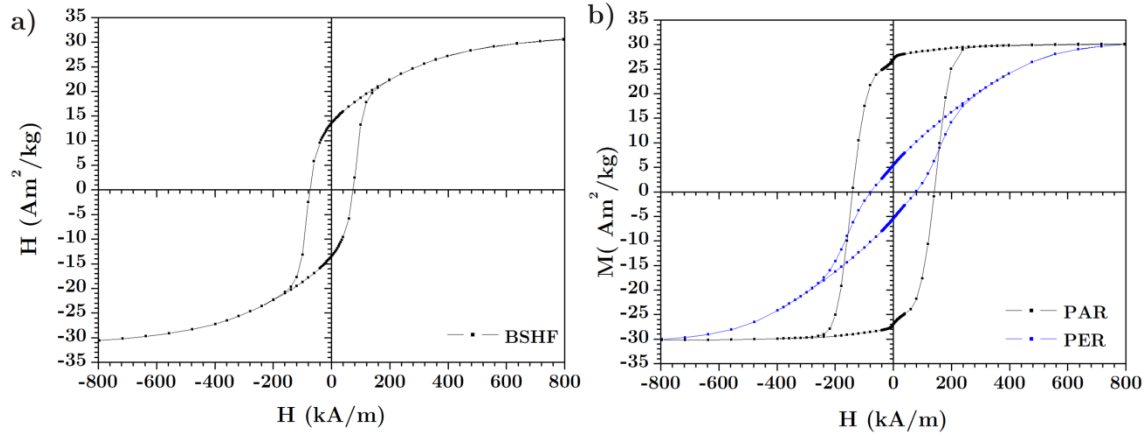


Figure 4.16: Magnetic hystereses for BSHF powder a) and for magnetically-orientated BSHF core nanoplatelets b). The orientated nanoplatelets were measured with field parallel (PAR) and perpendicular (PER) to the easy axis, which points perpendicular to the nanoplatelet.

To coat the BSHF core nanoplatelets with M layers, the stability of their suspension is required. The nanoplatelets tend to agglomerate due to van der Waals forces, and additionally due to magnetic forces. Agglomeration results in a decrease of the surface area available for the layer formation of the maghemite layer, and could promote the formation of the separate, homogeneously-nucleated nanoparticles, and generally decrease the homogeneity of the product. To prepare the stable suspension, the attractive forces agglomerating the nanoplatelets have to be overcome with the electrostatic repulsive forces. The nanoplatelets in the suspension have to display large zeta potential. Figure 4.17 shows a measurement of the zeta potential as a function of the pH suspension. The zeta potential is very high in acidic medium, exceeding 40 mV. The BSHF nanoplatelets were therefore dispersed in water at pH of 4.7 where the high positive ζ - potential provides strong repulsive forces between the nanoplatelets. The suspension remained completely stable as long as the pH remained below approximately 6.

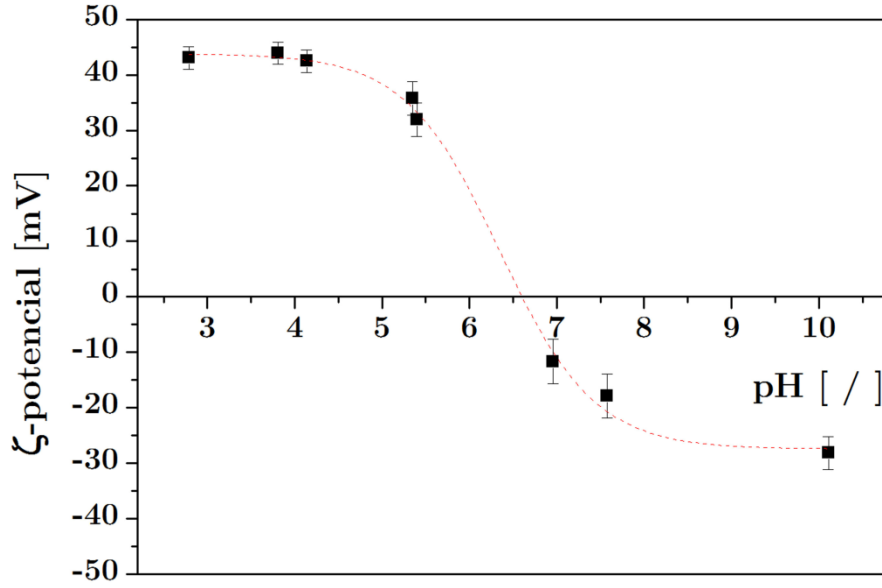


Figure 4.17: ζ -potential measurement of the aqueous suspension of BSHF nanoplatelets.

4.2.1.2 Properties of bi-magnetic nanoplatelets

The BSHF core nanoplatelets were coated with the maghemite (M) layer of different thicknesses using the controlled co-precipitation method [72, 76]. The thickness of the deposited maghemite layer was controlled by varying the molar ratio between iron precursors and core nanoparticles or by coating the cores in two consecutive deposition steps (see Section 1.6.1. for details on the synthesis procedure). The composite nanoplatelets were marked as “CNPX.X, where X.X denotes the average maghemite layer thickness in nm.

In Figure 4.18 a) the XRD patterns of the composite nanoplatelets CNP1.9 and CNP2.5 are compared with the XRD pattern of BSHF core nanoplatelets and globular maghemite (M) nanoparticles with a size approximately 10 nm. After the coating with the M layers, the additional peaks appear in the XRD pattern of the composite nanoplatelets. The additional peaks correspond to a cubic spinel structure. The XRD pattern of the composite nanoplatelets is therefore composed of the peaks corresponding to two phases; hexaferrite and spinel ferrite. The spinel/hexaferrite ratio is larger for the CNP2.5 composite nanoplatelets with a thicker shell than for the CNP1.9 nanoplatelets. However, from the XRD analysis alone we could not determine if the spinel ferrite is magnetite or maghemite. Considering the reaction conditions used during the synthesis of the bi-magnetic nanoplatelets, which proceed under an inert atmosphere, the first spinel-ferrite phase formed is magnetite (Fe_3O_4). However, magnetite nanoparticles are prone to oxidation into the maghemite ($\gamma\text{-Fe}_2\text{O}_3$), when they are exposed to the ambient air [22].

To resolve between the two iron-oxides with a spinel structure, Raman spectroscopy was used. The Raman spectrum (Figure 4.18 b) of the maghemite nanoparticles shows bands at positions characteristic of iron oxide having a maghemite structure [22, 107]. There are three Raman active lattice vibrations that give rise to three bands having a broad structure [107]. The distinction between maghemite and magnetite is in the position of bands, which are in case of magnetite shifted to lower wavenumbers for at least 30 cm^{-1} [107]. The difference in bands positions is significantly larger than spectral resolution. Barium hexaferrite in principle exhibits 42 Raman active modes and a much richer spectrum compared to the iron oxides [27]. All of the bands present in a spectrum

of BSHF are characteristic for the barium hexaferrite structure [27]. The sample CNP1.9 shows an additional band at approximately 380 cm^{-1} which is absent in the spectrum of BSHF and is not characteristic for the barium hexaferrite structure. The additional band is very close to the maghemite characteristic band, present in the spectra of maghemite nanoparticles, positioned at 350 cm^{-1} . This band is the only one in maghemite that is not overlapping with bands of the hexaferrite structure. Further evidence of the maghemite presence is absence of a band in CNP1.9 at approximately 300 cm^{-1} , where a relatively strong band is usually observed in magnetite [107]. We believe that these results are a firm evidence that the spinel layer at the surface of the BSHF core nanoplatelets crystallizes as the maghemite.

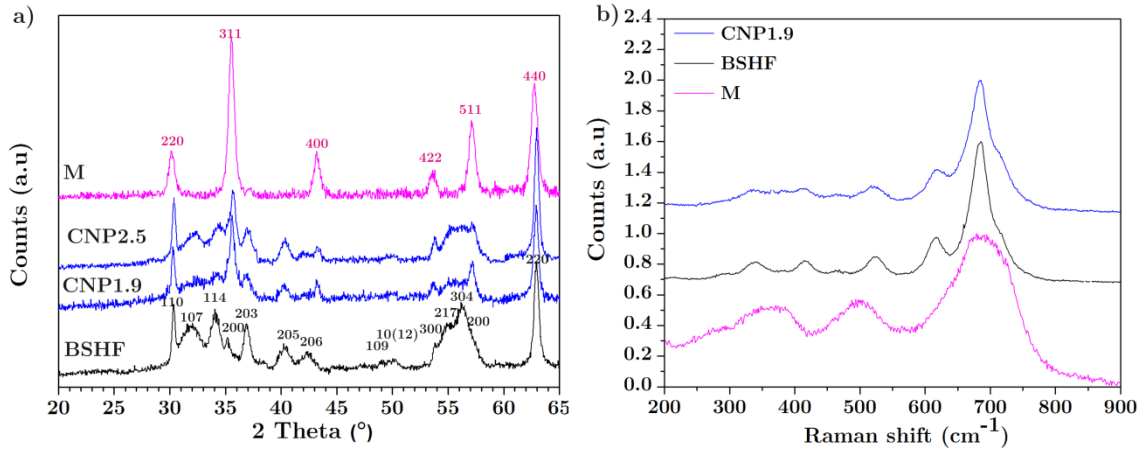


Figure 4.18: a) XRD pattern of the composite nanoplatelets CNP1.9 and CNP2.5 compared to XRD spectra of BSHF core nanoplatelets and XRD spectra of maghemite nanoparticles and b) Raman spectra of the maghemite nanoparticles (M), hexaferrite core nanoplatelets (BSHF) and the composite nanoplatelets (CNP1.9).

The structure of the CNP composite nanoplatelets was characterized using transmission electron microscopy (TEM). Figure 4.19 reveals that with coating, the composite nanoparticles retain the platelet shape of the cores (Figure 4.19 a)). Moreover, the high resolution imaging in TEM (HREM) and scanning-transmission electron microscopy (STEM) revealed that the composite nanoplatelets exhibit a sandwich-like structure, which can only be observed when they are orientated edge-on, with the basal surfaces parallel to the electron beam (Figure 4.19 b), c), e), and f)). Imaging of several hundred composite nanoplatelets reveals that each one is composed of a hexaferrite core (HF) sandwiched in between the two maghemite (M) layers. The detailed structure of the composite nanoplatelets was examined with an aberration-corrected STEM. Figures 4.19 e) and f) show an atomic-resolution high-angle-annular dark field (HAADF) STEM images of the composite nanoplatelets orientated with their HF cores along the $\langle 10-10 \rangle_{\text{HF}}$ direction and $\langle 11-20 \rangle_{\text{HF}}$ direction, respectively. The hexaferrite core is clearly resolved from the iron-oxide M surface layers.

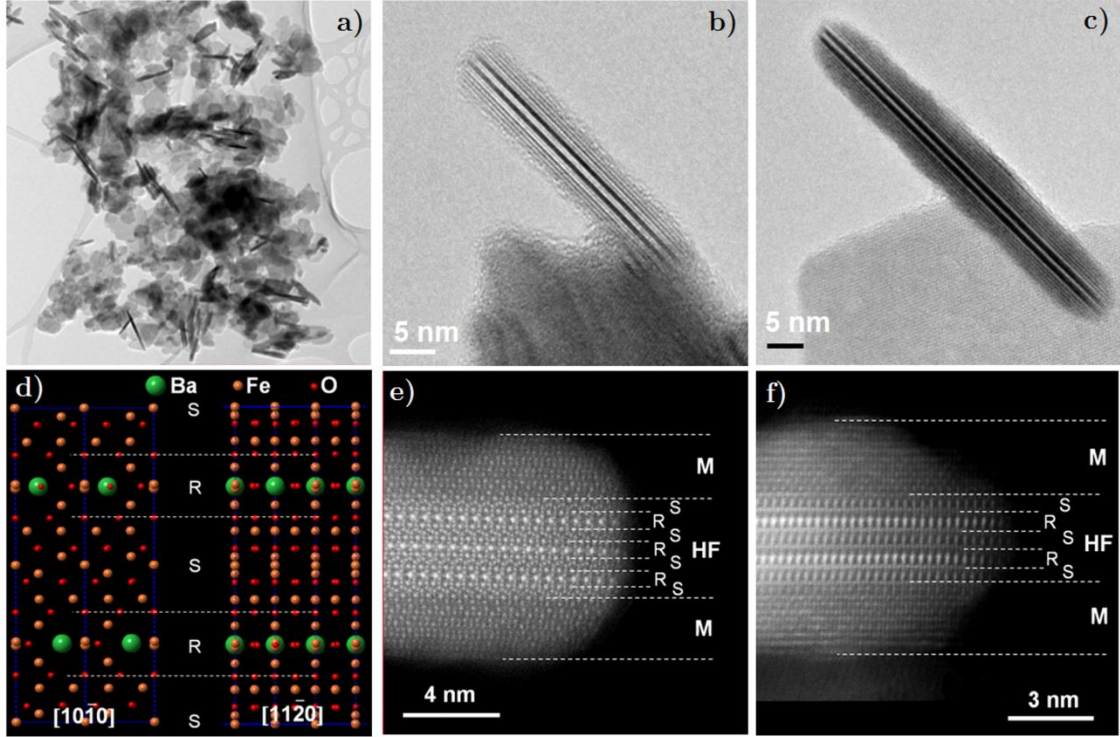


Figure 4.19: TEM image of the composite nanoplatelets in sample a) CNP1.9, HREM images of the composite nanoplatelets orientated edge-on, with basal planes perpendicular to the electron beam in sample b) CNP-1.9 and c) in sample CNP2.5, d) schematic presentation of hexaferrite structure, e) and f) HAADF STEM images of the composite nanoplatelets (sample CNP2.5) with the hexaferrite (HF) core orientated along $\langle 10-10 \rangle_{\text{HF}}$ e) and $\langle 11-20 \rangle_{\text{HF}}$ f).

In Figure 4.20 a) the experimental HAADF image is compared with a calculated image based on the HF and M atomic models. The projected structures (HF along $[10-10]_{\text{HF}}$ and M along $[101]_{\text{M}}$, only cations are shown) are superimposed over the experimental and simulated images in Figure 4.20 a). Intensity of the spot representing an individual atomic column on HAADF images depends on the column average atomic number Z ($I_{\text{HAADF}} \propto Z^2$) [108]. Therefore, the brightest spots in the Z-contrast images of the composite nanoplatelets represent the columns containing Ba^{2+} with $Z = 137$, the intensity of the columns containing lighter Fe^{3+} ions with $Z = 56$ is weaker and varies with their occupancy, while the O^{2-} ions with $Z = 16$ are not visible at all. In the HF structure the Ba^{2+} ions are situated in the middle of the hexagonal $(\text{BaFe}^{3+}_6\text{O}^{2-}_8)^{2+}$ “R” block, while Fe^{3+} occupy five crystallographic sites, i.e., tetrahedral ($4f_1$), octahedral ($12k$, $2a$, $4f_2$), and trigonal ($2b$) (the positions of Fe^{3+} sites are marked in Figure 4.20 a) [3, 25-27]. In the HAADF images of the composite nanoplatelet's HF core (Figure 4.20) the Ba columns alternate with Fe 2b columns making the row in the middle of the “R” block. The row of Fe $4f_1$ columns is at the transition from the “R” block to the cubic “S” ($\text{Fe}^{3+}_6\text{O}^{2-}_8$) $^{2+}$ block. Occupancy of each second column in the Fe $12k$ row is doubled resulting in the spots of alternating brightness. The HF core always terminates with the layer of Fe^{3+} ions at the $12k$ lattice sites, that is with the complete “S” block in the HF structure, which actually represents a (111) slice of the common spinel structure.

In the composite nanoplatelets the M layers grow epitaxially on both sides of the HF core. However, the iron oxide was never deposited onto the side surfaces of the cores. In

the $A[B]_2O_4$ spinel structure cations are distributed among tetrahedral (A) and octahedral (B) lattice sites (the positions of Fe^{3+} sites are marked in Figure 4.20 a)). In the spinel structure, the (A) sites are fully occupied by Fe^{3+} , while one third of the (B) sites remain unoccupied (structural formula: $(Fe^{3+})[Fe^{3+}_{5/3}\square_{1/3}]O_4$, where $\square$ stands for vacancy and round and square brackets represent tetrahedral and octahedral sites, respectively). As the HF structure terminates with the “S” block, which is actually a slice of the spinel structure, the HF structure of core could be simply extended by the M spinel layer. Usually, the structure of the M layer was slightly shifted along the interface due to the slight mismatch between both structures. The structural order in the surface layers seems to be worse than in the core. Stacking faults can be observed at close-packed (111) planes of the M layers. In the case presented in Figure 4.20 a), the stacking fault (denoted as SF) is formed in the surface layers at both sides of the HF core, four layers from the interface.

However, the formation of the SFs can be induced by the STEM imaging itself. The HF cores (including the terminating spinel “S” block at their surfaces) were fairly resistant to the electron beam and can be imaged for longer periods of time, without visible changes, even when the microscope was operated at 200 kV. On the contrary, the maghemite surface layers of the composites degrade relatively quickly under the electron beam. Therefore, the composite nanoplatelets were carefully imaged at 80 kV not to induce the formation of SFs.

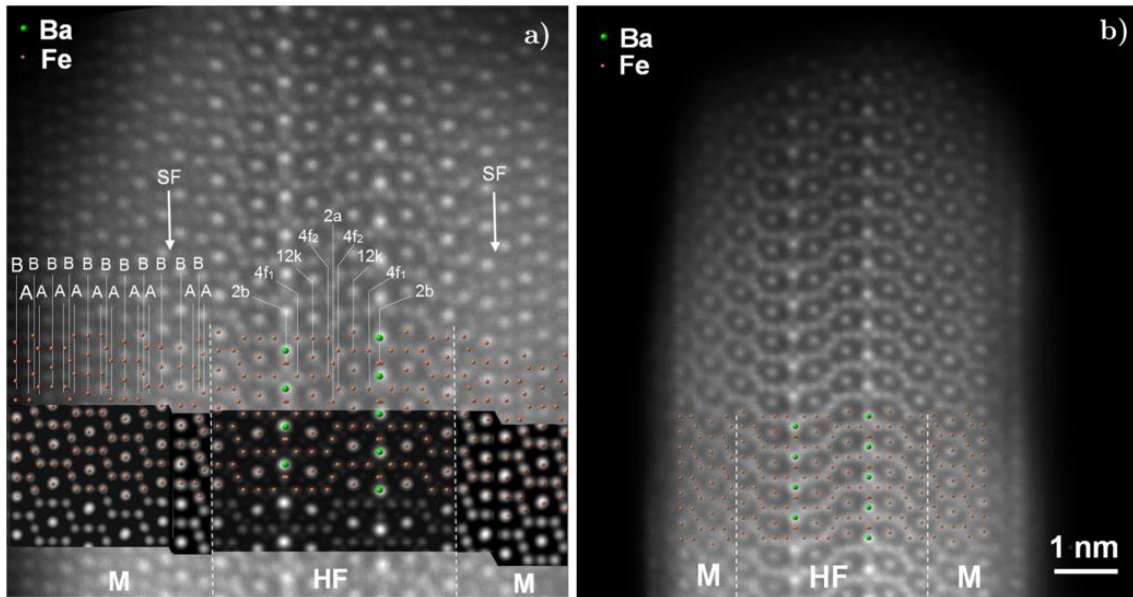


Figure 4.20: a) HAADF STEM images of the as-synthesized composite nanoplatelet (sample CNP-2.5) with superimposed calculated images for hexaferrite (HF) along $\langle 10\bar{1}0 \rangle_{HF}$ and maghemite (M) along $\langle 101 \rangle_M$ and b) of composite nanoplatelet (sample CNP-1.9) heated for 2 hours at 500 °C in air. The projected structures are superimposed over the images to illustrate the position of Ba^{2+} and Fe^{3+} ions. Different Fe lattice sites in the maghemite spinel structure (tetrahedral A and octahedral B) and in the hexaferrite structure (trigonal 2b, tetrahedral $4f_1$, octahedral 12k, 2a and $4f_2$ are marked in (a)). (SF denotes stacking fault).

With heating of the composite nanoplatelet at 500 °C for 2 h in air, the maghemite surface layers completely crystallize (Figure 4.20 b)). The interfaces between the HF core

and M layers are not resolved any more, as the outer-most spinel “S” block of the HF core continues into the maghemite surface layer without any visible discontinuity.

The thickness of the M layers covering the BSHF core nanoparticles was controlled by varying the ratio between the iron precursors and HF cores. When the Fe precursors were precipitated onto the core nanoplatelets in the Fe/HF molar ratio of 2.7, the M layer was 1.1 ± 0.1 nm thick (sample CNP1.1). With increasing the Fe/HF ratio, the M layer thickness increased: to 1.5 ± 0.1 nm at Fe/HF of 3.6 (sample CNP-1.5) and finally to 1.9 ± 0.2 nm at Fe/HF of 5.4 (sample CNP1.9, Figure 4.19 (b)). However, when the Fe/HF ratio was increased over 5.4, the supersaturation of the precipitating iron species was too high for heterogeneous nucleation of the precipitates at the surface of the core nanoplatelets. The high supersaturation resulted in the formation of separate, homogeneously nucleated M nanoparticles (marked with A in Figure 4.21 a)). To enable further increase of the thickness of surface layers nucleated at the core nanoplatelets, the coating process had to be conducted in two steps. CNP1.9 composite nanoplatelets with 1.9 nm thick maghemite layer, deposited in the first coating step (Fe/HF = 5.4) were thoroughly washed and re-dispersed in water. The CNP1.9 composites were then coated with an additional maghemite layer (Fe/HF = 2.6) in the second step. The thickness of the surface layers deposited onto the core nanoplatelets in the two-step process were 2.5 ± 0.2 nm (sample CNP2.5). Apart from the symmetric composites with equally-thick M layers on both sides, very seldom asymmetric composites with much thicker M layer at one side of the core nanoplatelet were found in the CNP2.5 sample (marked with B in Figure 4.21 a) and Figure 4.21 b)).

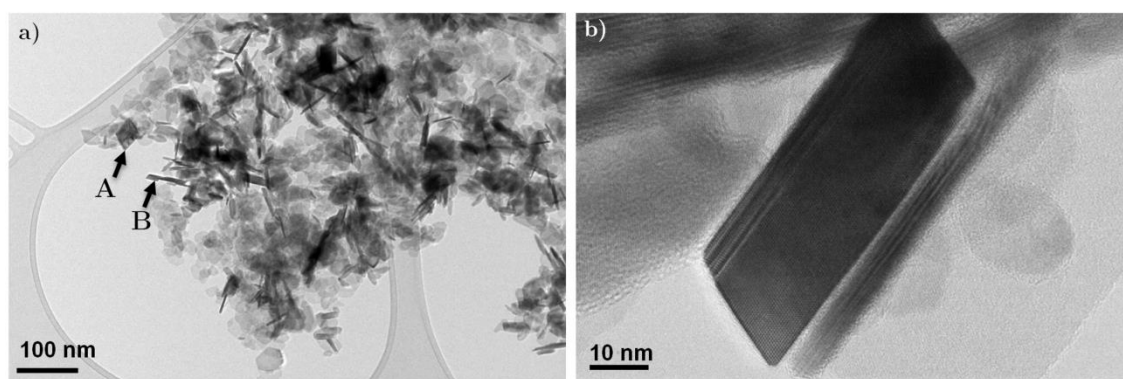


Figure 4.21: a) Representative TEM image of CNP2.5 sample and b) HRTEM image of asymmetric composite particles. (Homogeneous nucleated M nanoparticles marked as A and asymmetric composite nanoplatelets marked as B).

4.2.1.2.1 Room-temperature magnetic measurements

The magnetic properties of the hard-magnetic HF nanoplatelets can be strongly improved by coating with soft-magnetic maghemite layers [72]. The presence of the soft-magnetic M phase can contribute to the improved M_s , while coercivity is dominated by the hexaferrite phase. Moreover, it is expected that with varying the thickness of the M layer it is possible to tune the hysteresis loop of the bi-magnetic composite nanoplatelets to meet the requirements of specific application.

Magnetic properties of the HF nanoplatelets strongly depend on their orientation: the material is magnetically hard when measured perpendicular to the platelet and soft when measured parallel to the platelet (see Figure 4.16 b)). For the magnetic characterization

of such anisotropic particles it is desired to be oriented prior to the measurement. However, even the core nanoplatelets could be effectively oriented in the magnetic field (see Figure 4.16) the composite nanoplatelets could not be completely oriented as it could be seen in Figure 4.22. In the case of the composite nanoplatelets the M_R/M_S is significantly smaller than for the BSHF nanoplatelets. This implies that alignment of the composite nanoplatelets with the magnetic field is somewhat worse. This probably has two different origins. Firstly due to the increased M_S the magnetostatic interactions tend to increase, which leads to a considerable tendency to agglomeration, which can strongly influence the magnetic alignment. Although the steps were taken to minimize the aggregation (e.g., the nanoplatelets were coated with ricinoleic acid as the surfactant) it is difficult to completely prevent its agglomeration. Additionally, it should be taken into the account, that while the BSHF core has an out-of-plane easy axis, the soft-magnetic $\gamma\text{-Fe}_2\text{O}_3$ layers should have a tendency to lie in-plane due to the shape anisotropy. Therefore, the competition between these two anisotropies could result in a somewhat tilted easy axis, which could also affect M_R/M_S .

To avoid the problem of the unknown orientation, a low amount of the nanoplatelets was dispersed in a sucrose melt at $\approx 140^\circ\text{C}$. After the cooling to the room temperature, the solid was milled, pressed into cubes and measured in three directions using VMS. With dispersing the nanoplatelets into the nonmagnetic sucrose, the dipole-dipole interactions between the magnetic nanoplatelets, which also influence the shape of the hysteresis, were minimized. The uniaxial pressing into the cubes induced slight preferential orientation of the nanoplatelets. The hysteresis loops of the BSHF core nanoplatelets measured parallel to the direction of the pressing force (x-axis) were broader compared to those measured in the two perpendicular directions (y-axis and z-axis) for all the samples (Figure 4.23). It is known that the BSHF nanoplatelets display uniaxial magnetic anisotropy with easy axis perpendicular to the basal planes [3, 95]. The broader hysteresis measured in the pressing direction is therefore consistent with the preferential orientation of the BSHF perpendicular to the pressing direction. As the BSHF nanoplatelets, also composite nanoplatelets exhibit broader hysteresis loops measured in the pressing direction (Figure 4.23 c)-j). Therefore, it is reasonable to conclude that the easy axis is also pointing out of the plane in the case of the composites.

Figure 4.24 shows hystereses obtained by averaging the measurements in the three directions. From the comparison between the hysteresis of the BHFS and CNP nanoplatelets it is evident that the coating of the hard-magnetic BSHF nanoplatelets with soft-magnetic maghemite layers significantly improved their M_S .

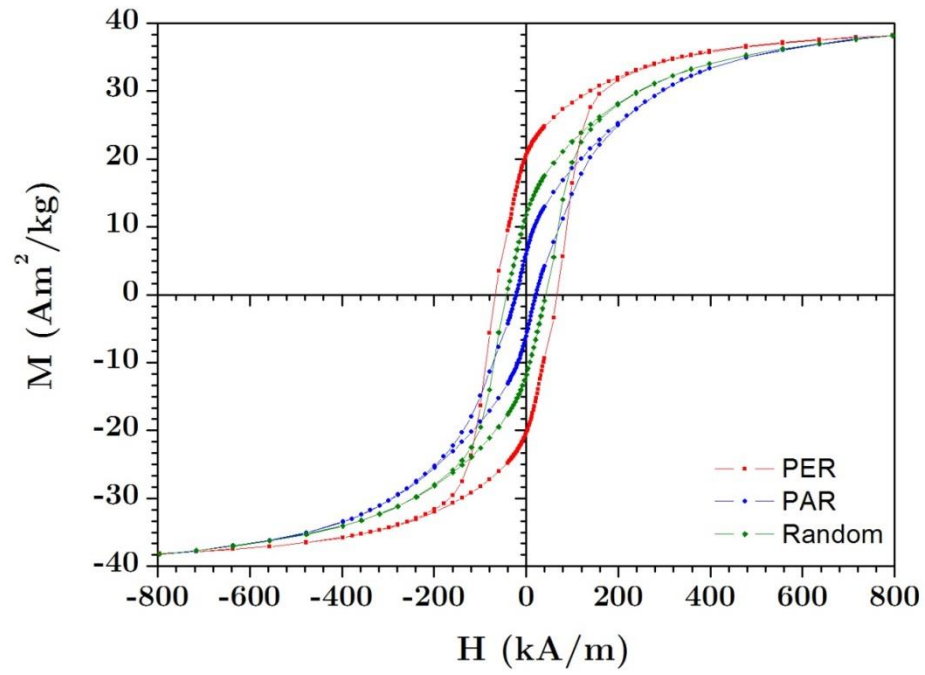


Figure 4.22: Magnetic hystereses for CNP1.1 composite nanoplatelets orientated randomly and parallel (PAR) and perpendicular (PER) with their basal surfaces to the applied field.

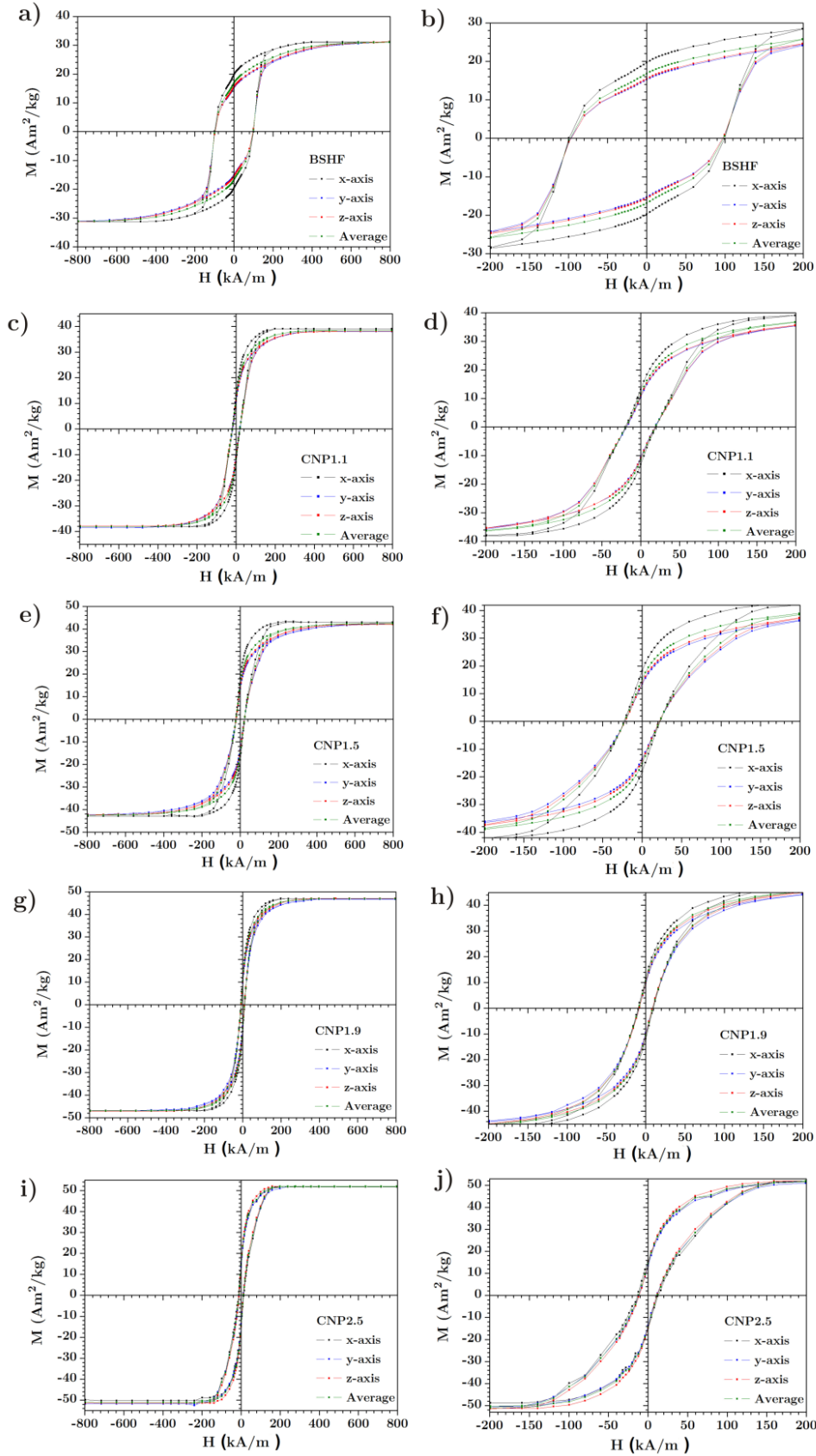


Figure 4.23: Magnetic hystereses for BSHF a) and b), CNP1.1 c) and d), CNP1.5 e) and f), CNP1.9 g) and h), and CNP2.5 i) and j) nanoplatelets. The nanoplatelets were dispersed in the nonmagnetic sucrose, pressed in the cubes and measured in the three directions (x-axis corresponds to the pressing direction).

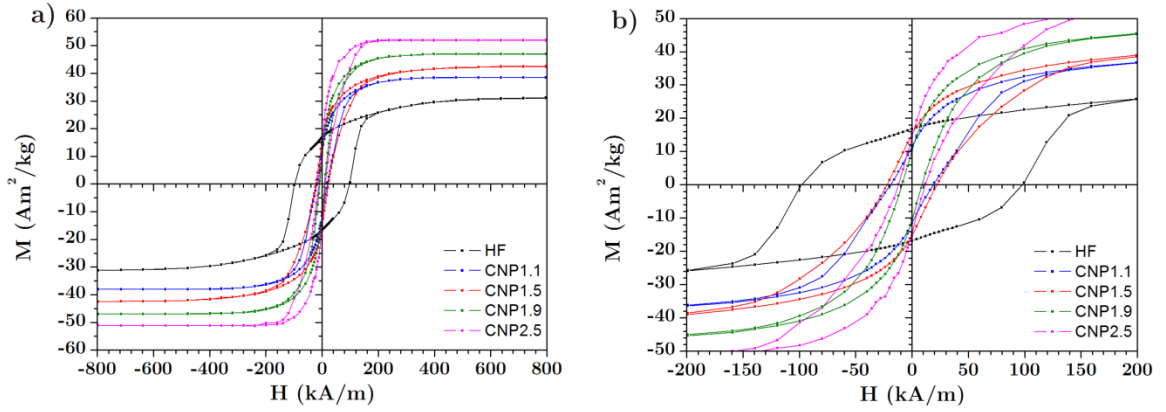


Figure 4.24: Average magnetic hysteresis of CNPX.X composite nanoplatelets in comparison to BSHF core nanoplatelets.

The M_S of the composite nanoplatelets ($M_{S(CNP)}$) increase proportionally to the thickness of maghemite layers (Table 4.6). Considering that $M_{S(CNP)} = w_{BSHF} \cdot M_{S(BSHF)} + w_M \cdot M_{S(M)}$ (mass fraction of w_{BSHF} and w_M were estimated from CNP dimensions and are given in Table 4.6), $M_{S(M)}$ of the layer can be estimated. The estimated values of $M_{S(M)}$ increase with increasing thickness of the maghemite layer from 52 Am²/kg to 68 Am²/kg. The estimated values are realistic M_S values for the nanosized maghemite. The volume of the individual maghemite layer in CNP1.9 composite nanoplatelets corresponds to the volume of globular maghemite nanoparticles of approximately 9 nm in size. The maghemite nanoparticles of a comparable size, synthesized with co-precipitation of Fe³⁺/Fe²⁺ ions, displayed $M_S \approx 66$ Am²/kg (hysteresis shown in Figure 4.25).

Table 4.6: Estimated composition and magnetic properties for BSHF core and CNP nanoplatelets. The mass fraction w of the two phases was estimated assuming the core nanoplatelet with an average width of 42 nm and average thickness of 3.5 nm.

Code	Estimated composition		M_S (Am ² /kg)	M_R (Am ² /kg)	H_C (kA/m)	$M_{S(M)}$ (Am ² /kg)
	w_{BSHF} (/)	w_M (/)				
BSHF	1	0	31	16.8	97.5	/
CNP-1.1	0.66	0.34	38	11.6	18.8	52
CNP-1.5	0.56	0.44	42	15.3	22	56
CNP-1.9	0.50	0.50	47	10.5	8.7	63
CNP-2.5	0.43	0.57	52	14.2	12	68

The nanoplatelets, except CNP2.5 (Figure 2.23 and 2.24), display a single-phase hysteresis loop proving that the two magnetically different phases, the hard-magnetic HF and soft-magnetic maghemite are exchange coupled in the CNPs.

The presence of any significant amount of the non-coupled maghemite phases would lead to a characteristic constricted shape of a hysteresis loop (Figure 4.25). The typical kinks resulted from separate switching of magnetic moments of both phases in the reverse field [19]. To demonstrate the degree of the magnetic coupling between the two magnetically different materials, the hysteresis of the composite nanoplatelets was compared with a physical mixture of the hard-magnetic (BSHF nanoplatelets) and the soft-magnetic M phases. As the soft-magnetic phase, the globular M nanoparticles with the size 9.7 ± 1.5 nm, were chosen. The volume of the M nanoparticles was comparable to that of the M layers in CNP1.9 composite nanoplatelets. For preparing the physical

mixture, the two types of magnetic particles were dispersed in sucrose as in the case of the BSHF and CNP nanoplatelets. Then the sucrose powders with magnetic nanoparticles were mixed together in an $M/BSHF$ mass ration of 1, corresponding to the estimated composition of the CNP1.9 composite nanoplatelets. Figure 4.25 shows hystereses for the hard-magnetic BSHF core nanoplatelets, soft-magnetic maghemite (M) nanoparticles and corresponding physical mixture (BSHF+M). Red dashed loop represents the sum of magnetizations at given (H) for both magnetically different phases (Sum). The loop was calculated using the formula $M_{mix}(H_i) = 0.5 M_{BSHF}(H_i) + 0.5 M_M(H_i)$. The sample BSHF+M shows a characteristic constricted loop, revealing two incoherent phases, which magnetize independently [19]. At the saturated state, the magnetic moments of the two separated magnetically different phases in the mixture are pinned at the same direction. When the magnetic field is reduced, the magnetic moments of the soft phase in the mixture start to rotate first since they are not pinned by the magnetic moments of the hard-magnetic phase as in the case of the composite. This results in a relaxation of the magnetic moments of the soft-magnetic phase. At the $H = 0$ the magnetic moments of the soft-magnetic phase are randomly orientated, while the magnetic moments of the hard-magnetic phase are still partially orientated. Further decreasing of the magnetic field (towards the H_c) results in a complete relocation of the magnetic moments in the hard-magnetic material. The difference in the relaxation of the magnetic moments in the magnetically different phases resulted in the occurrence of typical kinks [19].

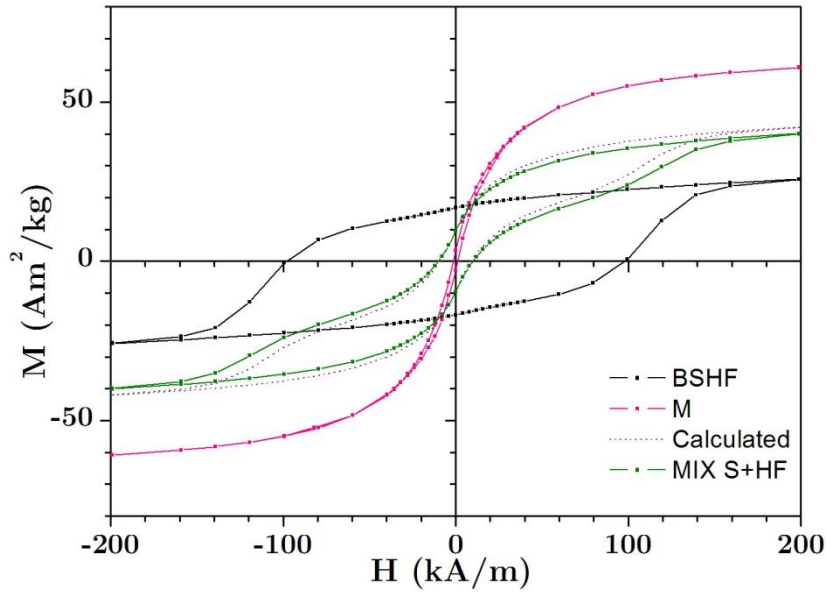


Figure 4.25: Magnetic hysteresis of BSHF core nanoplatelets, superparamagnetic maghemite nanoparticles (M) and their physical mixture and calculated hysteresis.

The slightly constricted loop was only observed for the CNP2.5 sample (Figure 2.23 and 2.24). The constriction could be the result of a too thick maghemite layer. However, the critical thickness below which the soft-magnetic phase is rigidly coupled with the hard-magnetic phase is generally considered roughly twice the width of a domain wall in the hard phase [16, 17, 25]. The width of the domain wall in the bulk barium hexaferrite is 14 nm [26], which is significantly thicker than the thickness of the maghemite layers of the CNP2.5. The observed slight constriction of the hysteresis for the CNP2.5 was

therefore ascribed to low content of the asymmetric composite nanoplatelets with several tens of nm thick maghemite layers on the surface of the cores.

The magnetic measurements showed that the M_s of the BSHF nanoplatelets was significantly increased with deposition of the maghemite layer onto their surface. Even the composite nanoplatelets (except CNP2.5) displayed the single-phase hysteresis loop, indicating the rigid exchange coupling between the two magnetically different phases, their remanence (M_R) and coercivity (H_C) were relatively low. The H_C of the composites drastically decreased compared to the H_C of the core nanoplatelets already when the thinnest maghemite layer was deposited (CNP1.1). With a further increase in the layer thickness the H_C was sporadic and relatively small.

4.2.1.2.2 Influence of the epitaxial spinel layers on magnetic properties of the hexaferrite core

Generally, in the case of the bi-magnetic composite nanoparticles combining magnetically hard and soft phases, the presence of the soft magnetic phase contributes to the improved M_s , while the H_C is dominated by the hard-magnetic phase. The result is a broad hysteresis loop, with improved energy product ($|BH_{MAX}|$) [20, 109].

When the core nanoplatelets were coated with the maghemite layer, the decrease in H_C was non-proportionally large. By rigid coupling between the two phases, it would be expected that the hard-magnetic core would dominate the H_C . However, the H_C of CNP1.1 decreased for ~80 %, even when the content of the soft-magnetic maghemite was only ~33 %. This suggests that the magnetic properties of the core changed when the epitaxial maghemite layers were deposited onto their surfaces. The properties of the core can be changed due to the internal stresses induced in the core by the deposited epitaxial maghemite layers. The expected mismatch between the two structures at the interface ((0001)_{HF} || (111)_S) is, however, relatively small.

To study how the epitaxial layers influence the magnetic properties of the BSHF core nanoplatelets, the zinc-ferrite layers were deposited onto the surface of the cores (sample ZnCNP). The bulk zinc ferrite ($ZnFe_2O_4$) is paramagnetic at room temperature, as the tetrahedral A sites of its normal spinel structure are almost exclusively occupied by the non-magnetic Zn^{2+} [3, 110]. The experiment would therefore demonstrate the influence of the internal stress induced in the hexaferrite core by the nonmagnetic epitaxial layers. However, with decreasing the size in the nano-range the zinc ferrite becomes weakly ferrimagnetic as a significant proportion of the Fe^{3+} ions exchanges sites with the Zn^{2+} ions, i.e., it adopts a partially inverted spinel structure [111]. Globular zinc-ferrite nanoparticles of approximately 8 nm are superparamagnetic with M_s of approximately 8 Am²/kg. With annealing at temperatures above approximately 400 °C the structure of zinc ferrite rearranges to the equilibrium “bulk” state and the nanoparticles became paramagnetic [112].

The zinc ferrite was deposited using the same deposition method as in the case of the synthesis of the CNP1.9 composite nanoplatelets, except that $FeCl_2$ was replaced with $ZnCl_2$.

The TEM analysis (Figure 4.26) revealed that also in the case of the deposition of the zinc ferrite layer, the composites retain a platelet shape of the cores. The HRTEM imaging of the composite nanoplatelet reveals that the BSHF core nanoplatelet is positioned in between the two layers. The EDXS analysis revealed that each nanoplatelet contains Zn. Elemental mapping recorded by EDXS in STEM (Figure 4.27) clearly showed the presence of Zn in the layers.

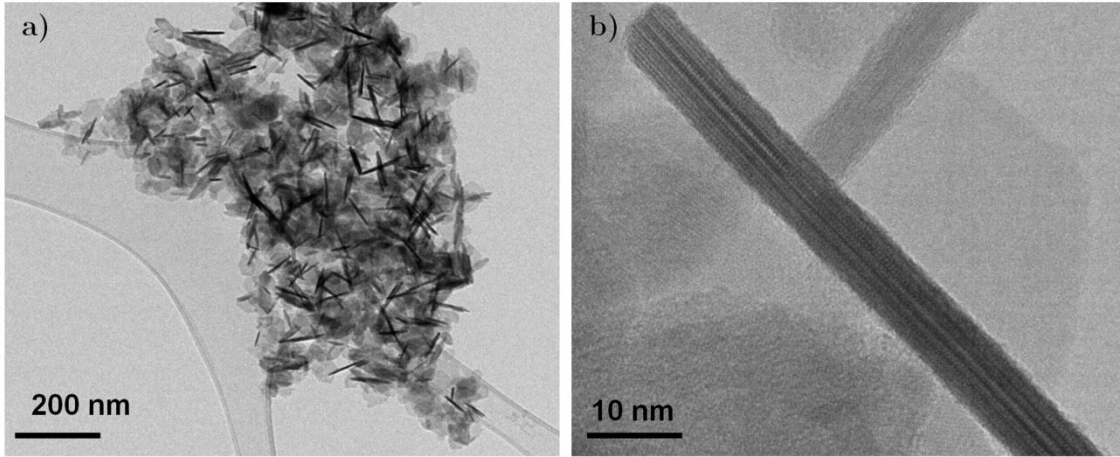


Figure 4.26: TEM (a) and HRTEM (b) images of ZnCNP nanoplatelets.

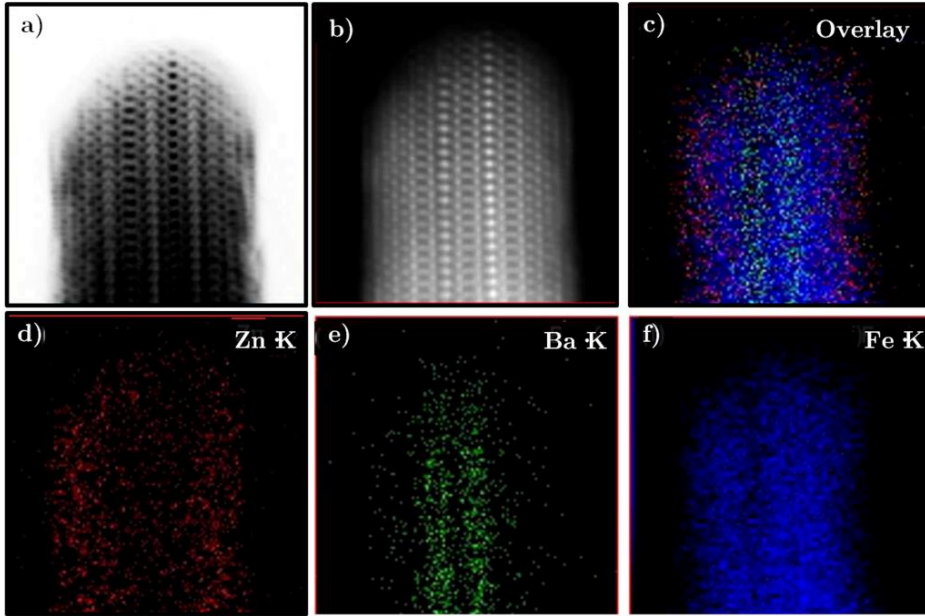


Figure 4.27: BF a) HAADF b) STEM images and corresponding EDXS elemental mappings c)-f) of the ZnCNP composite nanoplatelets orientated with its hexaferrite (HF) core along $\langle 11-20 \rangle_{\text{HF}}$. The sample was annealed for 2 hours at 500 °C.

The hysteresis loop of the composite nanoplatelets ZnCNP with approximately 1.9 nm thick zinc-ferrite layers is presented in Figure 4.28. The ZnCNP sample showed a single-phase hysteresis. The M_s of the as-synthesized ZnCNP decreased to 22 Am²/kg compared to the BSHF core nanoplatelets. The decrease in the magnetization indicates that the deposited layer is weakly magnetic. Estimation of the M_s of zinc ferrite layer considering its mass fraction in the composite ($w_{\text{layer}} \approx 0.5$) gave $M_{s(\text{layer})}$ of approximately 13 Am²/kg. If the decrease in H_C would not be related to the structural changes in the core induced by the epitaxial layers, the deposition of the weakly-magnetic zinc ferrite epitaxial layers would have a very small influence. However, the measurements revealed that even though the zinc-ferrite layers are weakly magnetic, they had a pronounced influence on the H_C of

the composite nanoplatelets. The H_C was decreased for $\approx 55\%$ compared to the BSHF core nanoplatelets.

With annealing of the ZnCNP sample at 500°C the M_s of the composite further decreased, almost to the half of the M_s of the BSHF cores. This indicates that the zinc-ferrite layers became close to paramagnetic after annealing, while the H_C did not change. The magnetic measurements showed that even when the zinc-ferrite layers were nonmagnetic, they had a pronounced influence on the H_C of the composite nanoplatelets, which can only be related to the structural stress induced in the cores by the epitaxial surface layers.

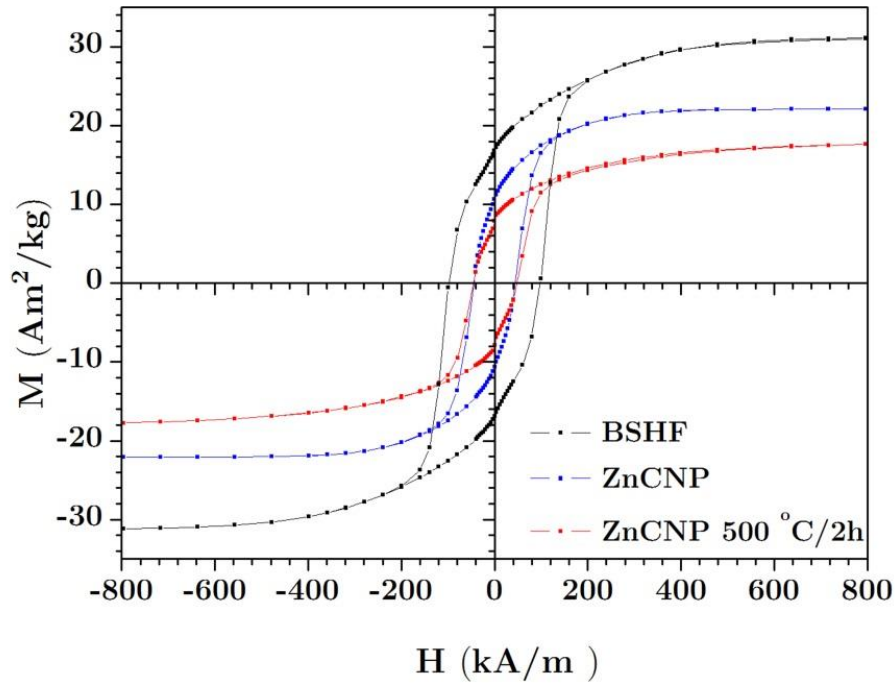


Figure 4.28: Comparison between the hysteresis loops of BSHF core nanoparticles and ZnCNP composite nanoplatelets synthesized by deposition of zinc ferrite onto the BSHF cores.

4.2.1.3 High-temperature magnetic measurements

The influence of the epitaxial maghemite layers on the magnetic properties of the BSHF core nanoplatelets was further investigated by high-temperature VSM measurements. To minimize the growth and excessive agglomeration at the high temperatures, the nanoplatelets (BSHF cores and CNP1.1 composite nanoplatelets) were coated with a silica shell prior to the measurement. The temperature dependence of M measured at 16 kA/m for BSHF core and CNP composite nanoplatelets is shown in Figure 4.29 a). The M vs T curve for the BSHF core nanoplatelets monotonically decrease with increasing temperature, without any upturn below the Curie temperature T_C , which would indicate the growth of the nanoplatelets during heating. TEM/STEM analysis confirmed that the size of the BSHF nanoplatelets does not significantly increase during heat treatment. Upon cooling from 550°C , the cool-down curve is below the worm-up curve, which indicates that the magnetic properties of the BSHF nanoplatelets irreversibly changed. Comparison of hysteresis loops measured before and after the heating experiment (Figure 4.29 b)) showed the lower M_s and M_R after heating, but increased H_C . The T_C determined from the inflection point of the worm-up curve (the minimum of dM/dT curve) is ≈ 342

°C, which is lower than in the case of the bulk hexaferrite. Pure bulk hexaferrite displays T_C of approximately 450 °C [113], however with decreasing the particle size, the T_C also decreases. The partial substitutions of Fe^{3+} ions with non-magnetic Sc^{3+} also decrease the T_C . Moreover, the T_C of BSHF nanoplatelets is also much lower than the T_C reported for the pure barium hexaferrite nanoplatelets of the comparable size, which is approximately 368 °C [114].

The M vs. T curve of the CNP1.1 composite nanoplatelets is significantly different compared to the BSHF curve. In the case of the composites, the curve does not drop to zero up to the final temperature of 550 °C. After the decrease related to the T_C of the HF core, the M phase remains significant due to the presence of the maghemite layer. The maghemite displays T_C at a temperature above 550 °C. Actually the T_C between ≈ 550 °C and 710 °C was reported for the maghemite, however, it usually transforms into the thermodynamically more stable hematite before reaching T_C [22]. In the CNP1.1 curve, the small upturn, around 430 °C, can be observed in the warm-up curve. The upturn could appear due to the thickening of the individual maghemite layer deposited on the surface of the BSHF core nanoplatelets (see below). The thickening of the M layers and improved crystallinity should reflect in an increased magnetization of the maghemite and therefore in increased magnetization of the composite. However, the magnetization of the CNPs decreased after the heating (Figure 4.29 c)). After the heating, the CNP1.1 composite nanoplatelets display a single hysteresis loop with decreased M_R and H_C compared to the hysteresis obtained after the heating. Comparison between the hysteresis loops of the BSHF and CNP1.1 nanoplatelets obtained before and after the heating reveals that change in the magnetic properties is significantly larger for the CNP1.1 composite nanoplatelets than for the BSHF core nanoplatelets.

The T_C estimated for the hexaferrite cores of CNP1.1 from the inflection point of the M vs. T worm-up curve was ≈ 311 °C, which is significantly lower than the T_C of the BSHF core nanoplatelets.

The T_C is an intrinsic property reflecting the magnetic structure of the material. If the deposition of the M layer does not influence the magnetic properties of the cores, the T_C corresponding to BSHF in the composite should remain the same as for the BSHF nanoplatelets. However, the results showed that the T_C of the BSHF cores significantly decreased after epitaxial growth of the maghemite layers at their basal surfaces. The decrease in the T_C and the difference in the changes in the magnetic properties with heating of the CNP composite and the BSHF nanoplatelets indicate that the magnetic properties of the BSHF core nanoparticles are strongly influenced with epitaxial maghemite layers.

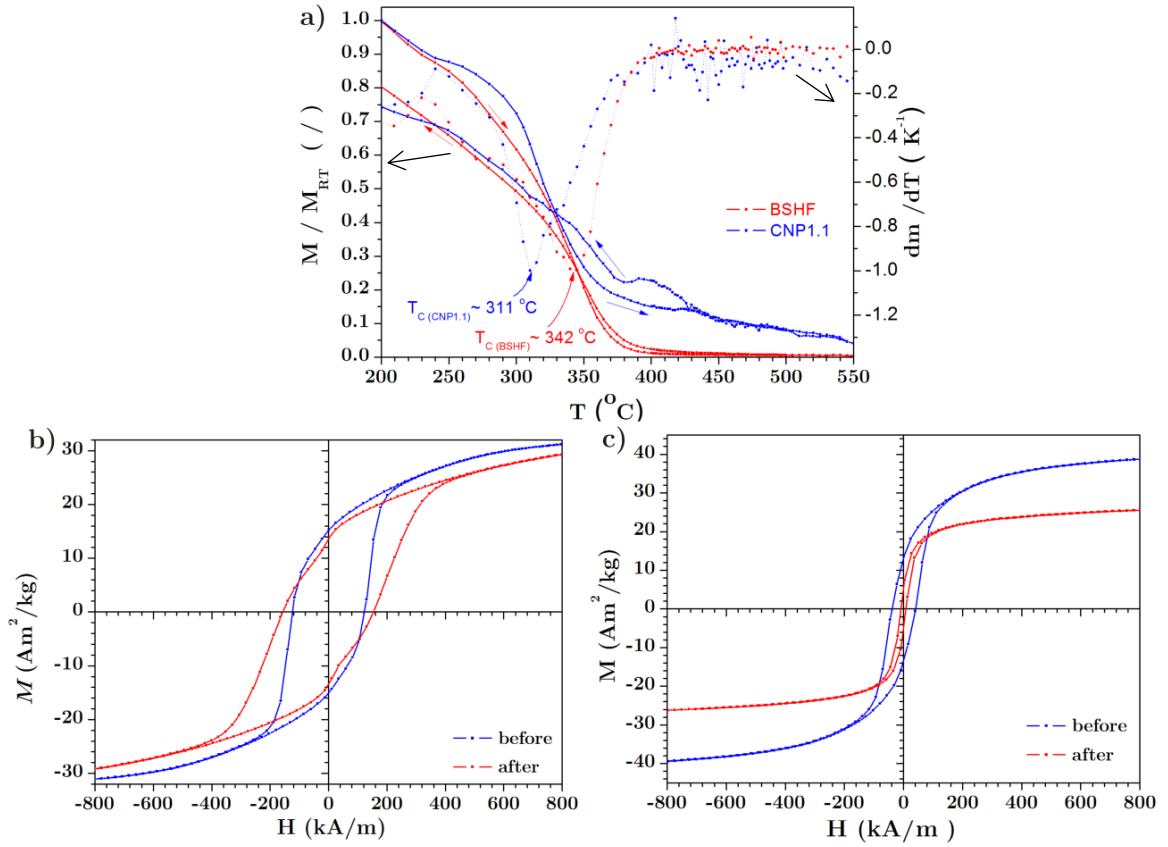


Figure 4.29: a) High temperature measurements of BSHF and CNP1.1 nanoplatelets and room temperature magnetic hysteresis of b) BSHF core and c) CNP1.1 composite nanoplatelets measured before and after high temperature measurements.

4.2.1.4 Temperature annealing of the CNP composite nanoplatelets

During the high temperature magnetic measurements the samples could change. For example, it is known that the maghemite changes to the hematite, which could result in a decrease of the M_s . However, if the maghemite transformed into the non-magnetic hematite, only the M_s should be decreased, while the H_C should be close to the value of the BSHF core. Moreover, with heating the composite, I expected that any local tensions be diminished and therefore the H_C of the composite would increase.

To explain the change of the magnetic properties of the composite nanoplatelets with the heating, the composites were annealed at different temperatures and analyzed after each annealing step. The uncoated CNP1.9 composite nanoplatelets were heated for 2 hours at different temperatures, ranging from 300 to 600 °C, in ambient air. To minimize the direct contact between them, the CNP1.9 nanoplatelets were dispersed in the Al_2O_3 powder, prior to the annealing.

At temperatures above 500 °C, the maghemite usually transforms into the non-magnetic and thermodynamically more stable hematite. However, the XRD pattern of the CNP1.9 heated for 2 hours at 400 and 500 °C (Figure 4.30 a)) are similar as for the as-synthesized CNP1.9 composite nanoplatelets. The XRD pattern of the composite nanoplatelets is composed of the peaks that correspond only to the two constitutive materials: the HF and the M. The Raman spectroscopy also confirmed that after the annealing the CNP1.9 nanoplatelets still contained only HF and M phases. Raman spectra of the composite nanoplatelets annealed at 400 and 500 °C are practically equal

as the spectrum of unheated CNP1.9 (Figure 4.30 b)). The Raman is a relatively sensitive method and already a small amount of the hematite should be detected if present.

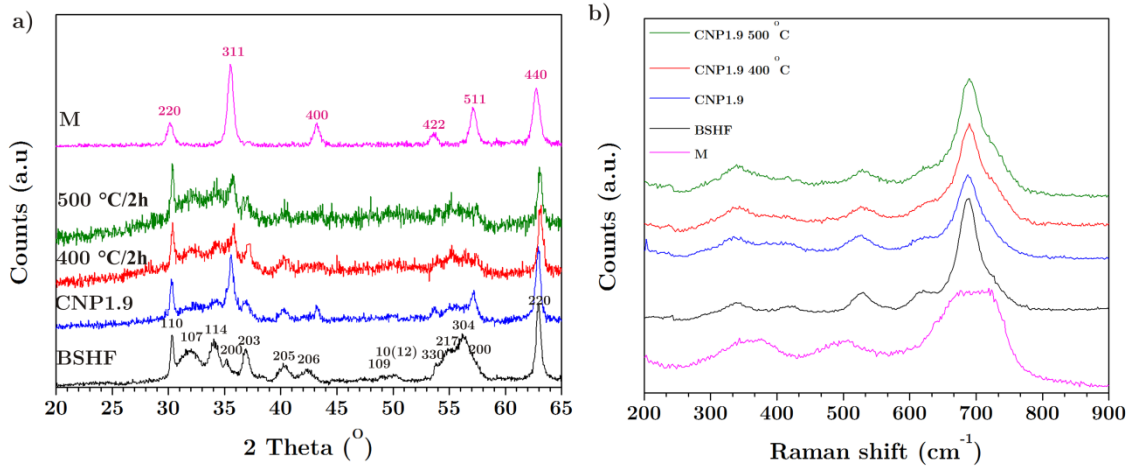


Figure 4.30: XRD spectra a) and Raman spectra b) of maghemite nanoparticles (M), hexaferrite core nanoplatelets (BSHF), as-synthesized and annealed composite nanoplatelets CNP1.1.

TEM and STEM analysis showed that asymmetric composite nanoplatelets with a very thick maghemite layer on the one side of the BSHF core nanoparticle appear already when the CNP1.9 was heated at 300 °C for 2 hours (Figure 4.31 a) and b)). The content of these asymmetric composite particles was very small. The majority of the nanoplatelets retained the original sandwich structure. Figure 4.31 c) shows the HAADF STEM image of the typical composite nanoplatelet after annealing at 300 °C. The interface between the two structures is clearly visible.

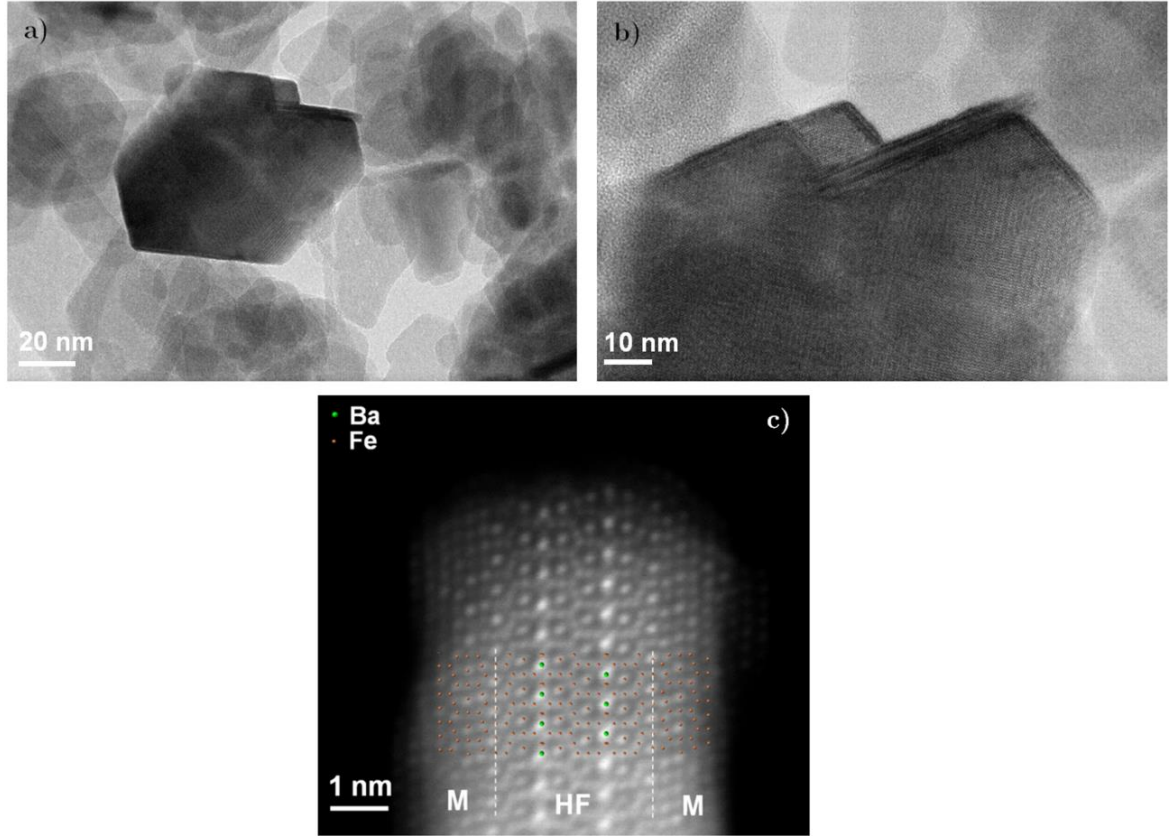


Figure 4.31: a) TEM and b) HRTEM images of the composite nanoplatelet with a very thick maghemite layer ($\langle 10\text{-}10 \rangle_{\text{HF}} \parallel \langle 101 \rangle_{\text{M}}$). HAADF STEM image of CNP1.9 composite nanoplatelet (c) ($\langle 10\text{-}10 \rangle_{\text{HF}} \parallel \langle 101 \rangle_{\text{M}}$) annealed at 300 °C for 2 hours. The projected HF and M structures are superimposed over the image to illustrate the position of Ba^{2+} and Fe^{3+} ions.

The TEM inspection of the CNP1.9 composite nanoplatelets annealed for 2 hours at 500 °C revealed that the amount of the asymmetric composite nanoplatelets with a thick M layer on the one side of the BSHF core increased (marked in Figure 4.32 a)). Figure 4.31 b)-d) shows HAADF STEM images of a typical asymmetric composite particle. With growth of the maghemite layer on individual nanoplatelets, the thickness of the maghemite at the majority of the composite nanoplatelets decreased. In the high-resolution STEM images the interfaces between the M and HF phases could not be resolved anymore (Figure 4.20 b)). Since the hexaferrite core nanoplatelets terminate with a structural S block, it simply continues with an M surface layer. The nanoplatelet does not display the sandwich composite structure anymore. It can be rather viewed as the uniform particle with a specific structure. In terms of the periodic stacking of two structural blocks: the Ba-containing $(\text{BaFe}^{3+}_6\text{O}^{2-}_8)^{2+}$ “R” block and the “S” $(\text{Fe}^{3+}_6\text{O}^{2-}_8)^{2+}$ block, the structure of the hexaferrite cores of the as-synthesized composite nanoplatelets can be presented as the “SRSRS” stacking. For a vast majority of the nanoplatelets after annealing at 500 °C the outer-most S block of the core is extended with two additional S blocks from the maghemite layer: SSSRSRSSS.

The as-synthesized composite nanoplatelets obviously decompose with the annealing above approximately 300 °C. The maghemite layer at the individual nanoplatelets exaggeratedly grows, while the thickness of the maghemite of the majority nanoplatelets

decreased. At the same time, the temperature was too low for any significant growth of the hexaferrite cores. The size of the cores was determined by measuring the width of the composite nanoplatelets. Because the nanoplatelets were agglomerated after the annealing, the size was estimated by measuring the largest dimension of any clearly visible nanoplatelet at the TEM images. With increasing the annealing temperature the average widths of the composite nanoplatelets somewhat increased, however the increase was small (Figure 4.33).

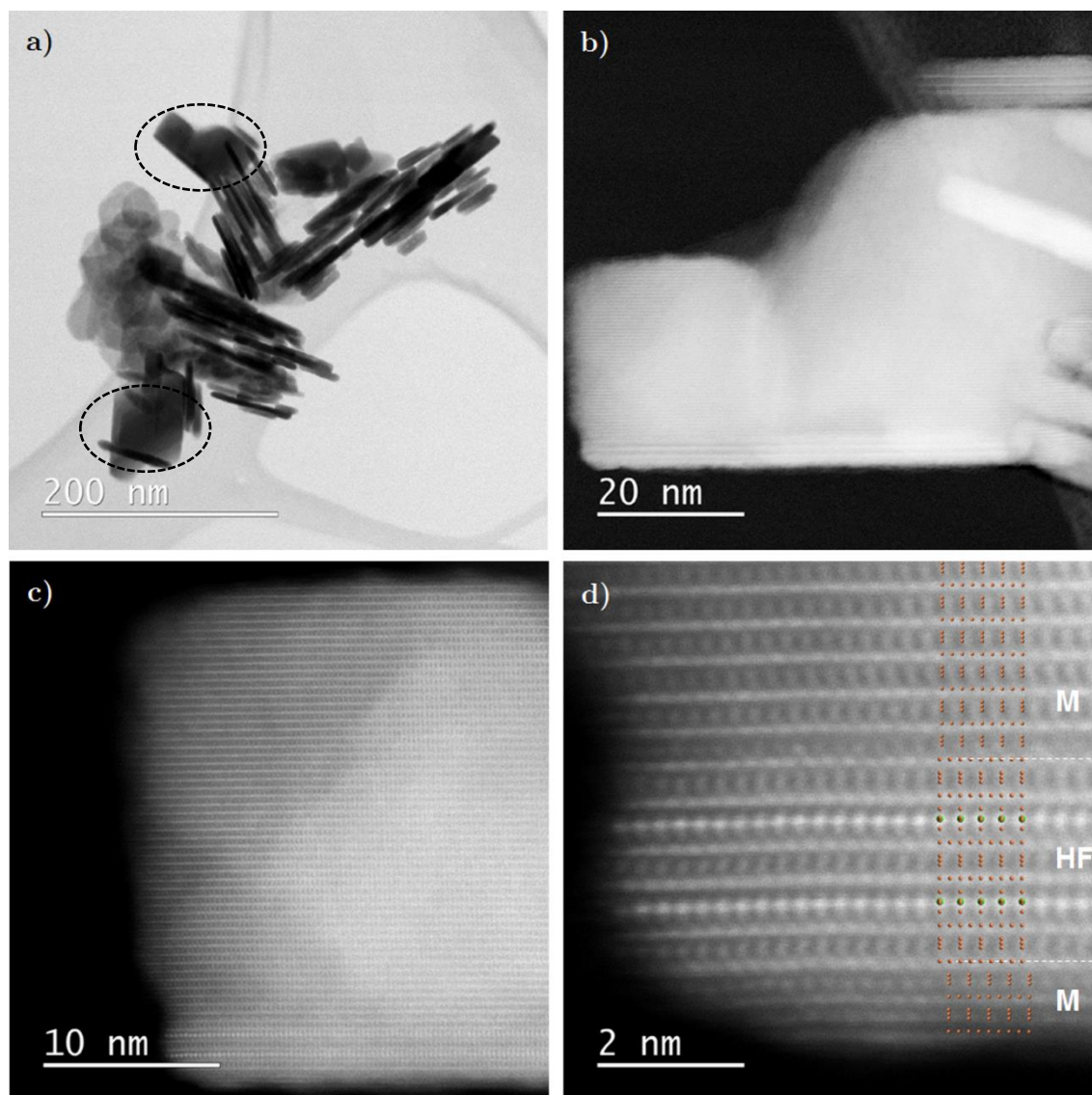


Figure 4.32: BF (a) and HAADF STEM (b-d) images of the CNP1.9 composite annealed for 2 hours at 500 °C. The asymmetric composite nanoplatelets with a thick M layer on the one side of the BSFH core are marked in Figure (a). The projected structures are superimposed over the image (d) to illustrate the positions of Ba^{2+} and Fe^{3+} ions.

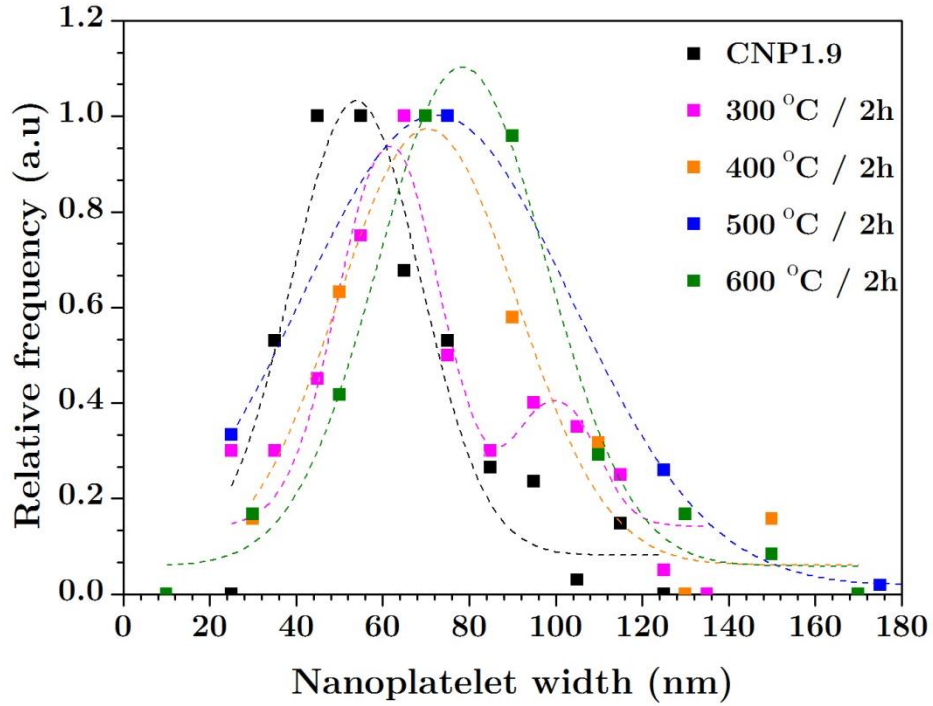


Figure 4.33: Distribution composite nanoplatelets widths measured from TEM images of the CNP1.9 composite annealed at different temperatures for 2 hours. Empirical size distributions were fitted with Gaussian curves.

Figure 4.34 shows the hysteresis loops of the annealed CNP1.9 nanoplatelets compared to the as-synthesized CNP1.9. The comparison showed that the M_S , M_R and H_C decrease with the increasing annealing temperature. Considering the TEM and STEM analysis we expected that with thickening of the maghemite layer and improved crystallinity, the M_S of annealed composites will increase. The decrease in the M_S would be consistent if the maghemite transformed to the non-magnetic hematite. However, the STEM, XRD and Raman spectroscopy analysis showed no changes in the composition of the composite nanoplatelets. The CNP1.9 nanoplatelets are still composed of the BSHF core nanoplatelets positioned in between two M layers. Therefore, the decrease in the magnetic properties of the annealed composite nanoplatelets must be related to the internal stress and the change in the magnetic properties of the BSHF core nanoparticles.

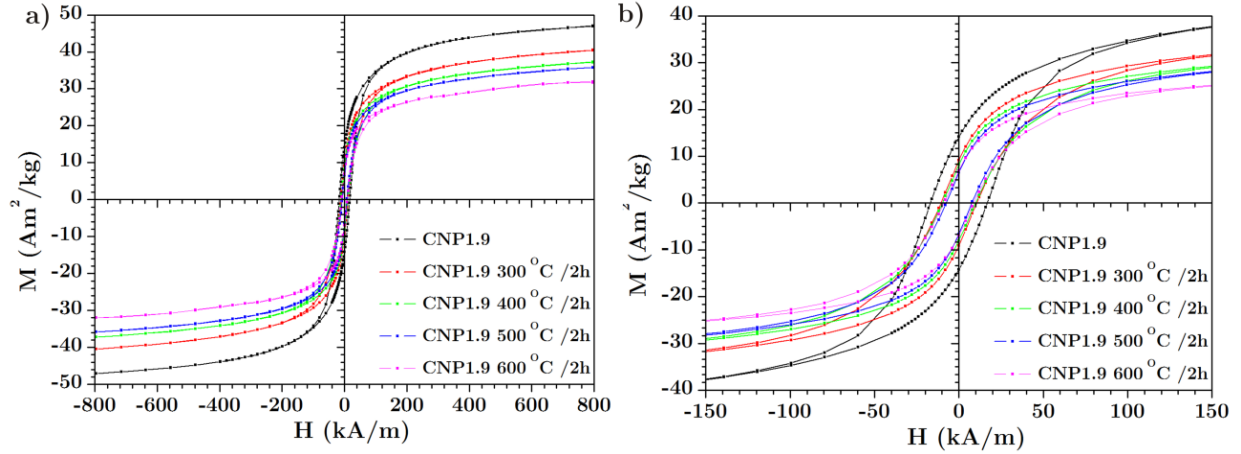


Figure 4.34: Room-temperature magnetic hysteresis loops for CNP1.9 measured after annealing the sample for 2 hours at different temperatures.

In conclusion, the magnetic measurements presented in this chapter revealed that the saturation magnetization M_s of the BSHF nanoplatelets can be significantly improved by deposition of epitaxial M layers. The M_s increased proportionally with the increasing thickness of the M layers. The composite nanoplatelets displayed a single hysteresis loop indicating that the magnetically-different materials are rigidly exchange coupled. However, despite the exchange coupling, the composites displayed a relatively low H_C .

We assumed that the decrease in the H_C of the nanoplatelets after the deposition of the layers resulted from the change of the magnetic properties of the cores, which were caused by a stress induced in the core by the epitaxial layers. To confirm this assumption the weakly-magnetic zinc-ferrite layers were deposited on the BSHF cores. The magnetic measurements showed that the weakly-magnetic layers strongly decreased the H_C . This indicated that the decrease of the H_C must be related to the internal stress induced in the hexaferrite core by the epitaxial layer. Moreover, the change in the magnetic properties of the hexaferrite nanoplatelets after deposition of the M layers was confirmed by high-temperature measurements. The Curie temperature of the hexaferrite cores of the composite nanoplatelets was lower compared to the as-synthesized BSHF core nanoplatelets.

4.2.2 Deposition of maghemite shell onto bismuth-titanate core nanoplatelets

I assumed that the controlled co-precipitation method, which was successfully used for the synthesis of maghemite/hexaferrite composite nanoplatelets, can also be used for the synthesis of other composite nanoparticles. By deposition of the maghemite shell on other core nanoparticles, completely new multifunctional composites combining magnetic material with materials of other functionalities would be synthesized [115-118]. To demonstrate the possibility of using the co-precipitation method for the synthesis of multifunctional composites, bismuth-titanate nanoparticles ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BIT) were used as cores.

BIT is a ferroelectric material, which exhibits a layered perovskite structure of Aurivillius type [33-35]. In the form of nanoparticles it appears in a platelet shape. Combining the magnetic shell with the ferroelectric core would be beneficial for controlling the orientation of ferroelectric nanoplatelets in the suspension with an applied

magnetic field. Moreover, such composite nanoparticles can also be used as building blocks for the preparation of magnetoelectric composites [23, 118-120].

4.2.2.1 Bismuth titanate core nanoplatelets

The BIT nanoplatelets were hydrothermally synthesized at 200 °C [87]. Figure 4.35 a) shows a representative TEM image of BIT nanoplatelets revealing its platelet morphology. According to the measurements from the TEM images, the nanoplatelets were 10-180 nm wide and 15-25 nm thick (Figure 4.35 b) shows the distribution of nanoplatelets' widths). Figure 4.35 c) represents a HRTEM image of the BIT core nanoparticle orientated along [010] of its tetragonal structure; that is with its large surfaces parallel to the electron beam. The HREM image of BIT is characterized by the largest periodicity of 1.64 nm, which corresponds to the (002)_{BIT} interplanar distances of its pseudotetragonal perovskite structure.

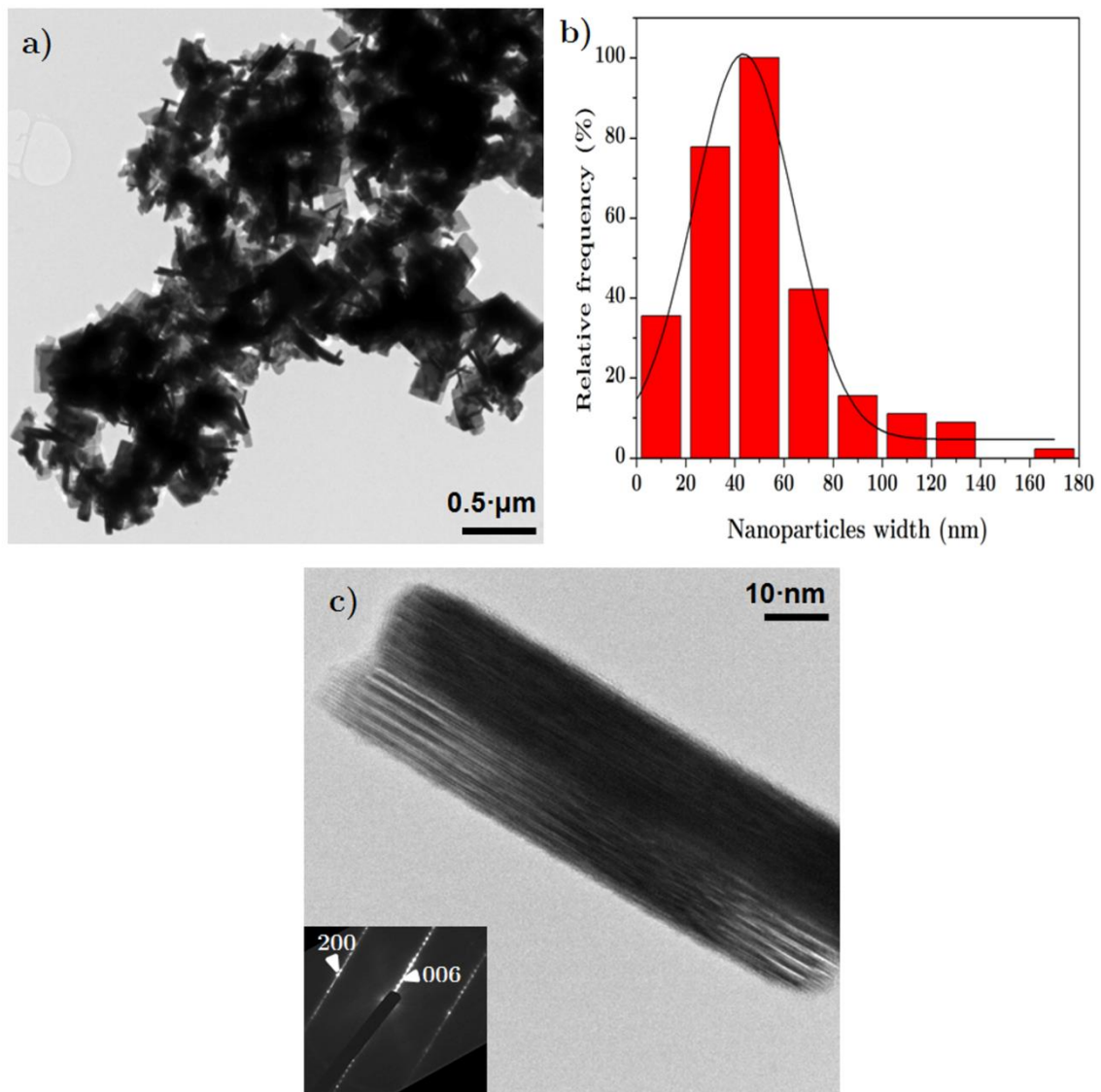


Figure 4.35: BIT core nanoparticles: a) representative TEM image, b) nanoparticle's width measured from TEM images, c) HRTEM image of the BIT core nanoparticle orientated along [010]_{BIT}, i.e. with its large surface parallel to the electron beam.

Figure 4.36 shows a XRD pattern of the BIT nanoplatelets. All the peaks were indexed according to a tetragonal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (PDF card No. 47-0398). It is expected that the nanoplatelets will show a ferroelectric orthorhombic structure. However, the difference between the tetragonal and the orthorhombic structures is too small to be resolved using XRD. Because of the large unit cell, the characteristic splitting of the peaks due to the transformation from the tetragonal cell ($a=5.46$ Å, $c=32.8$ Å) to the orthorhombic (SG B2ab (41), $a=5.448$ Å, $b=5.411$ Å, $c=32.8$ Å) could not be seen. The ferroelectricity of the nanoplatelets was therefore not confirmed.

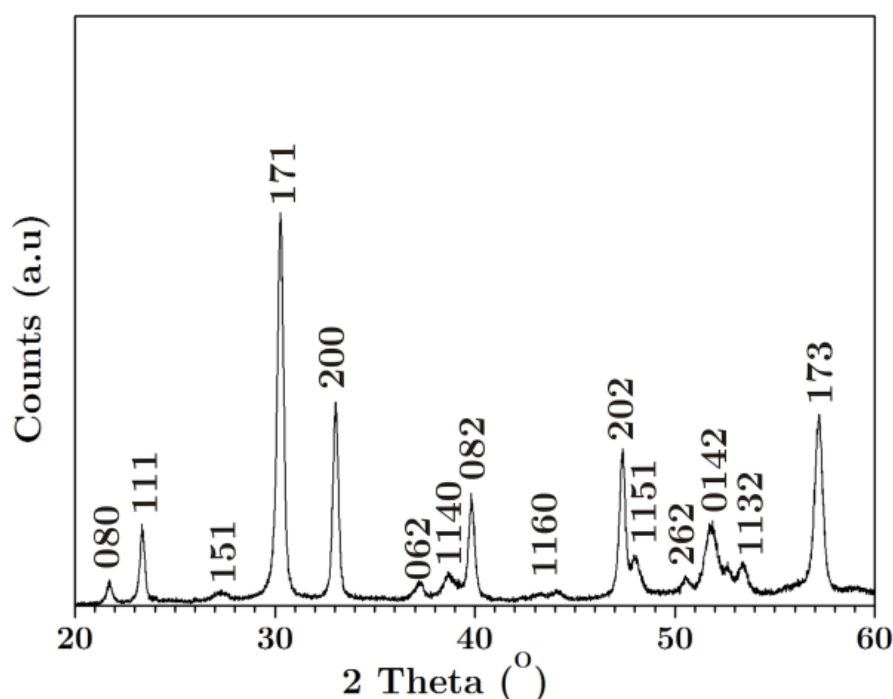


Figure 4.36: XRD pattern of BIT nanoplatelets.

To deposit the shell onto the BIT nanoplatelets the preparation of the stable aqueous suspension is required. The agglomeration of the nanoplatelets due to the attractive van der Waals forces was prevented with electrostatic repulsive forces as in the case of the BSHF cores. From the electro-kinetic measurement it was observed that the BIT nanoplatelets exhibited a large negative ζ -potential, enabling their colloidal stability over a broad region of pH above approximately 5 (Figure 4.37).

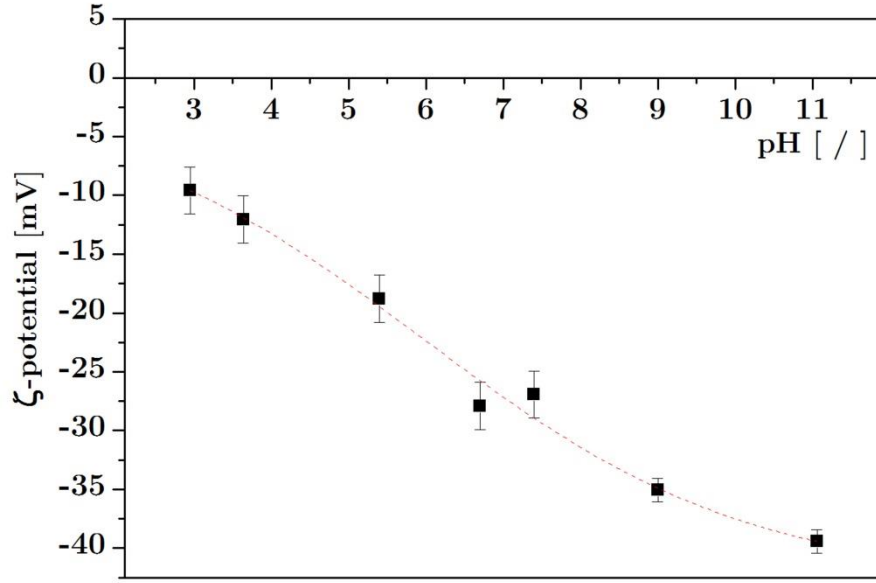


Figure 4.37: ζ -potential measurement of the aqueous suspension of BIT nanoplatelets.

4.2.2.2 Deposition of maghemite shell onto the surface of BIT core nanoplatelets

For the coating of the BIT core nanoparticles with maghemite shell (sample FBIT) the same conditions were selected as in the case of the successful synthesis of bi-magnetic composite nanoplatelets (Section 4.1.). First, the Fe precursors were dissolved into aqueous suspension of the BIT core nanoplatelets heated at 60 °C under the argon atmosphere. After the suspension was maintained at the pH of 2.2 for 10 minutes, allowing thermal hydrolysis of the released Fe^{3+} ions and formation of $\gamma\text{-FeOOH}$, the $\text{Mg}(\text{OH})_2$ was admixed. The addition of the hydroxide resulted in a gradual increase of the pH and precipitation of Fe^{2+} ions (Figure 4.38). The pH of 5.6, where the Fe^{2+} ions precipitate, was reached in approximately 10 minutes. After approximately additional 20 minutes the final pH value of ≈ 8 was reached. The reaction mixture was maintained at the final pH for 2 h. The product was then separated and washed for several times with distilled water. The course of the increase in pH after the addition of $\text{Mg}(\text{OH})_2$ in the BIT suspension was very similar as recorded in the case of deposition of the maghemite onto the hexaferrite cores.

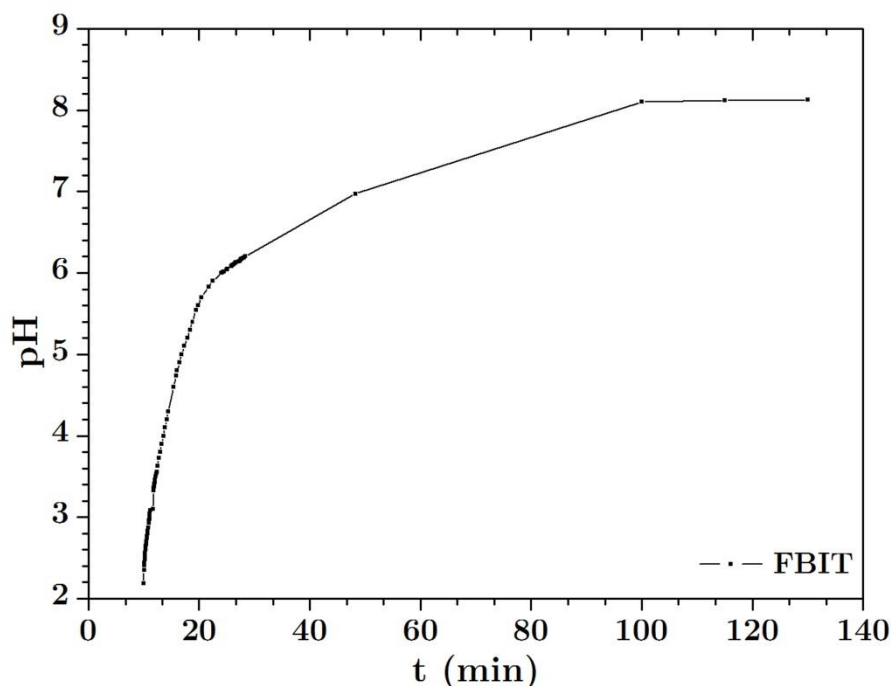


Figure 4.38: The increase of pH with time after $\text{Mg}(\text{OH})_2$ was admixed into the reaction mixture during preparation of the FBIT sample.

Figure 4.39 a) shows a representative TEM image of the FBIT sample. The detailed observation reveals that separate, small, approximately 5 – 10 nm large nanoparticles are attached on the surfaces of the BIT nanoplatelets (Figure 4.39 b) and c)). EDXS analysis of the coated FBIT composite nanoplatelets showed besides Ti, Bi, and O also the presence of Fe. The HRTEM analysis (Figure 4.39 c)) revealed that the small nanoparticles on the surface of the core nanoplatelets are amorphous. The SAED recorded on the nanoplatelet with the small nanoparticles showed only the reflections that can be indexed according to the pseudotetragonal structure of BIT (Figure 4.39 d)).

Beside the BIT nanoplatelets with attached amorphous nanoparticles, large agglomerates of particles of separate secondary phases have been observed (Figure 4.39 e)). The agglomerates contain two types of nanoparticles: approximately 50 nm long and 10 nm wide elongated nanoparticles and smaller spherical nanoparticles, approximately 10 nm in size. The corresponding SAED pattern (Figure 4.39 f)) reveals the formation of $\alpha\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$ phases.

Due to the poor crystallinity of the iron-rich secondary phases the XRD showed only peaks corresponding to the BIT (not shown).

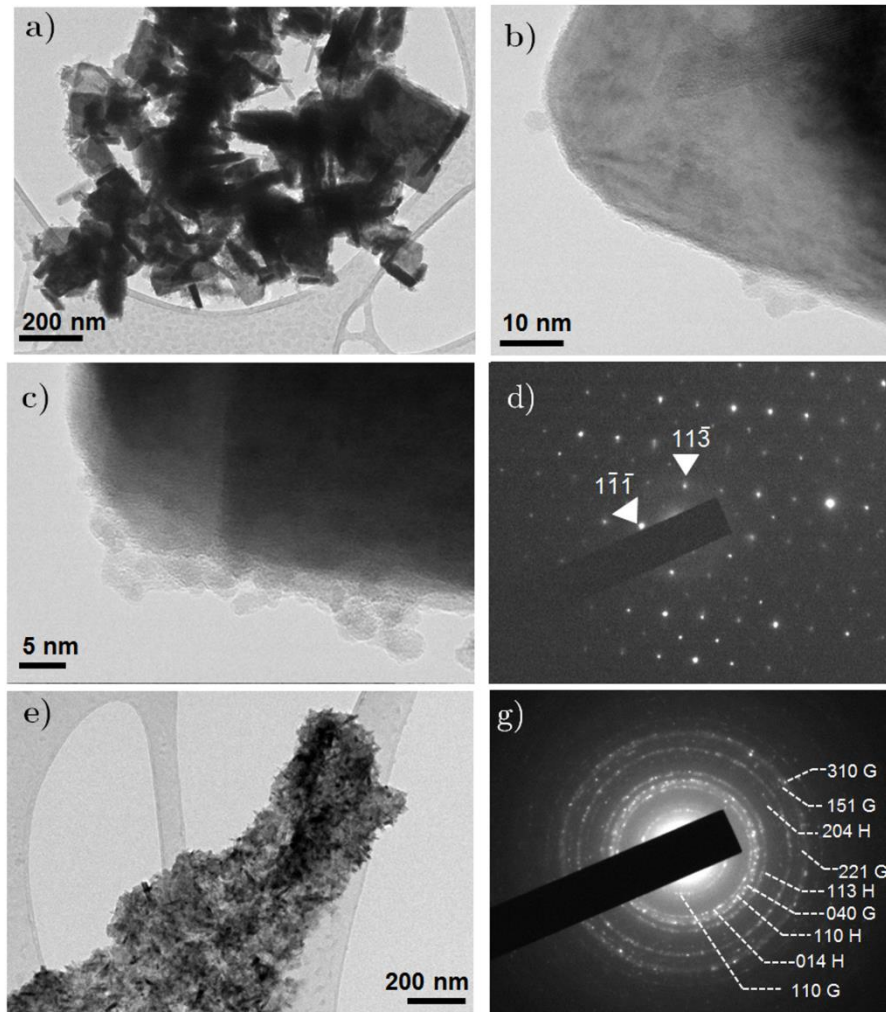


Figure 4.39: Representative images of the FBIT sample: TEM images a), b), HREM c) with a corresponding SAED pattern d). The SAED pattern was indexed according to the tetragonal perovskite structure along $[211]_{\text{BIT}}$. Figure (e) shows TEM of agglomerate of separate Fe-rich nanoparticles with corresponding electron diffraction g) which was indexed according to the structures of goethite (G) and hematite (H).

Magnetic measurements revealed that the FBIT sample was weakly magnetic with M_s of $1.2 \text{ Am}^2/\text{kg}$ (Figure 4.40). Compared to the BIT nanoplatelets, which display diamagnetic behavior. The M_s was significantly lower than expected for precipitation of the iron in the form of maghemite. If we take into account that all the reactants would precipitate in the form of the maghemite, the M_s should be approximately $8 \text{ Am}^2/\text{kg}$. The low measured M_s is consistent with TEM analysis, which revealed that the FBIT sample contains BIT nanoplatelets covered with amorphous nanoparticles and non-magnetic secondary $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ phases.

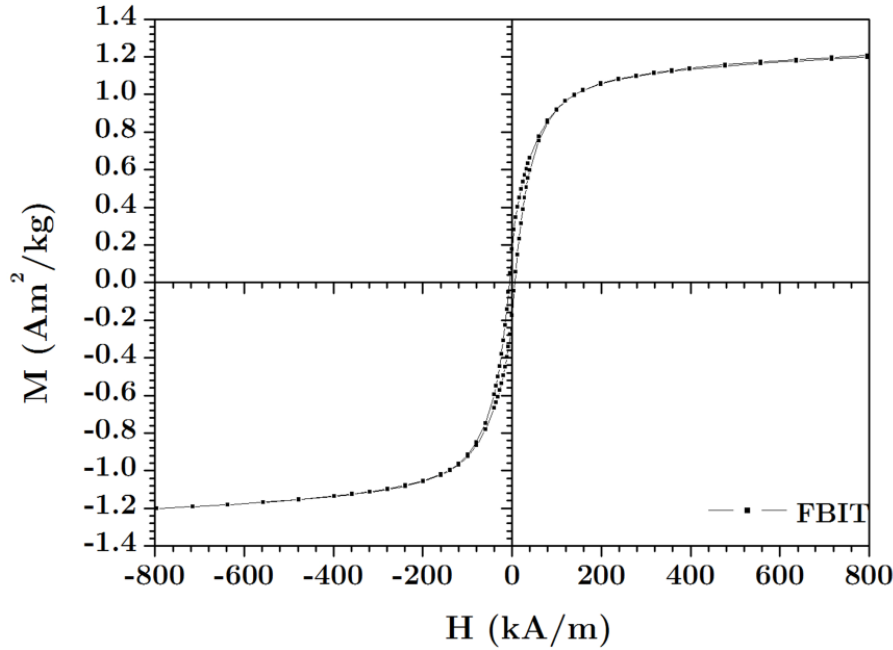


Figure 4.40: Magnetic hysteresis of the FBIT sample.

The coating of the BIT nanoplatelets with maghemite proceeded under the same reaction conditions as the synthesis of the bi-magnetic composite nanoplatelets. Therefore, we expected that the BIT nanoplatelets would be covered with the maghemite shell. However, the TEM analysis showed the small amorphous nanoparticles attached to the BIT core nanoplatelets and the separate, homogeneously nucleated particles of the secondary phases α -Fe₂O₃ and α -FeOOH. This is much different to the case of the bi-magnetic composite nanoplatelets, where iron-oxide always deposited exclusively as the maghemite, either in the form of epitaxial layers, or in the form of separate, well crystalline octahedral particles, when the concentration of the iron precursors was too high (Section 4.2.1).

There could be many explanations for the formation of the amorphous nanoparticles. The first reason could be related to the structural differences between the two phases. In the case when the HF nanoplatelets were used as the cores, the maghemite always appeared in the form of epitaxial layer grown exclusively on the basal surfaces, where the structural similarity between the two structures enables the formation of the low energy interface. The maghemite was also successfully deposited on the amorphous silica core nanoparticles [76].

The second reason which could obstruct the crystallization of the maghemite in the presence of BIT is partial dissolution of the core nanoplatelets in the reaction suspension or chemical reaction of the cores with the reactants. Those two possibilities will be presented later in Section 4.2.2.3.

In the first part of the investigation I focused on the subsequent treatment of the material, which would enable crystallization of the amorphous nanoparticles attached to the BIT cores. To promote the crystallization into the magnetic maghemite the FBIT samples were further hydrothermally treated or annealed at temperatures above 500 °C.

4.2.2.2.1 Hydrothermal treatment of FBIT sample

In order to crystallize the amorphous Fe-rich nanoparticles attached to the surfaces of BIT nanoplatelets, the material after the deposition was subsequently hydrothermally treated for 1 hour at 160 °C or at 180 °C (samples FBIT- T/t , where T and t denote temperature and time, respectively). First, the pH of FBIT suspension was adjusted to pH = 11. Generally, the conventional co-precipitation synthesis of spinel iron-oxide nanoparticles proceeds at high pH (pH > 10) [22]. After the pH adjustment the suspension was sealed in a Teflon-lined autoclave and heated for 1 hour at the chosen temperature.

TEM analysis of the hydrothermally treated samples does not show any significant differences compared to the as-synthesized FBIT sample. The BIT nanoparticles are covered with small nanoparticles (Figure 4.41 a)). The HRTEM analysis of the sample FBIT-180/1 reveals that the nanoparticles on the surface of the BIT remained amorphous. Figures 4.41 b) and c) represent HRTEM images of the BIT core nanoplatelets covered with amorphous nanoparticles. The corresponding SAED pattern shows only reflections that can be indexed according to the pseudotetragonal structure of the BIT core orientated along $[010]_{\text{BIT}}$ (Figure 3.41 d)).

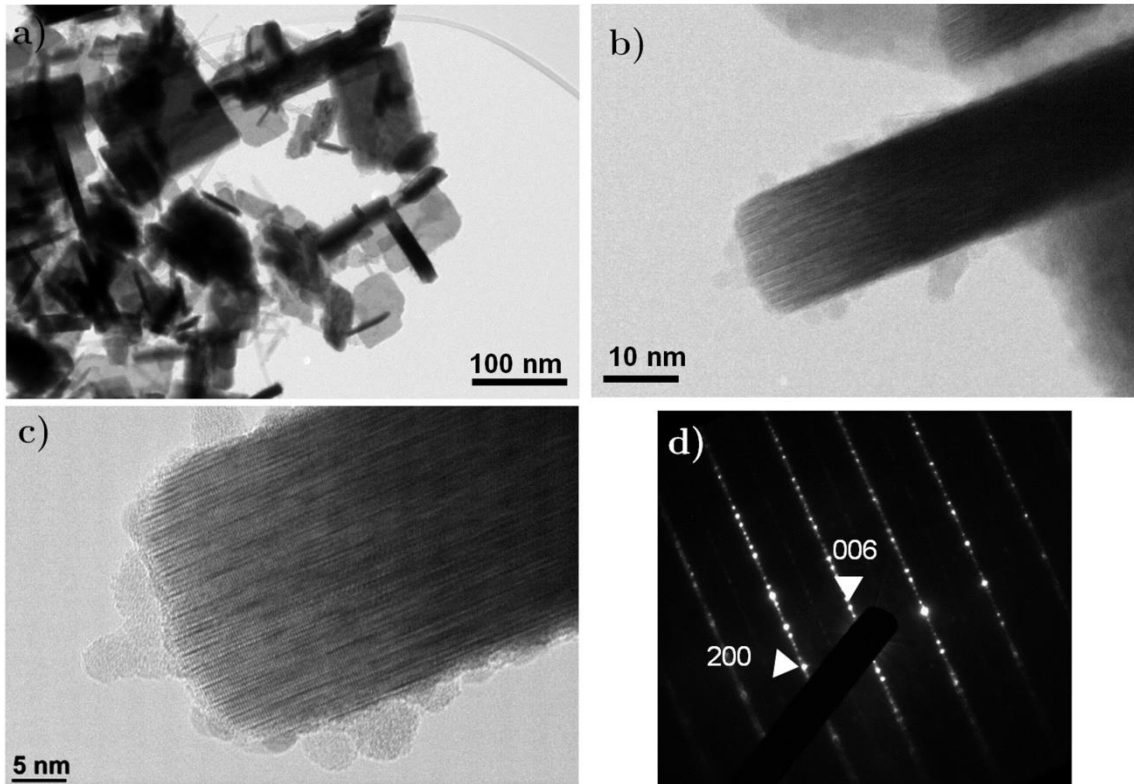


Figure 4.41: Representative TEM image a) and HREM image b) and c) with a corresponding SAED pattern d) of FBIT sample hydrothermally treated for 1 h at 180 °C. The SAED pattern was indexed according to the pseudotetragonal structure of BIT along $[010]_{\text{BIT}}$.

In the next step, the hydrothermal treatment of the as-synthesized FBIT sample was conducted under the reductive conditions (samples FBIT- T/t -HID). It is known that the crystallization of iron oxide in the form of magnetic spinel ferrite (magnetite) is favored under reductive conditions [22, 121]. To ensure reductive conditions hydrazine was added in the FBIT suspension prior to the hydrothermal treatment at 160 or 180 °C as the

reducing agent. The hydrothermal treatment proceeded as in the previous case. TEM analysis of the sample FBIT-160/1-HID treated at 160 °C showed no significant differences compared to the samples where hydrazine was not added. On the contrary, TEM analysis of the sample hydrothermally treated under the reductive conditions at 180 °C revealed growth of the BIT cores (marked in Figure 4.42 a)). However, the Fe-rich nanoparticles on the surfaces of the BIT nanoplatelets remained amorphous (Figure 4.42 b) and c)).

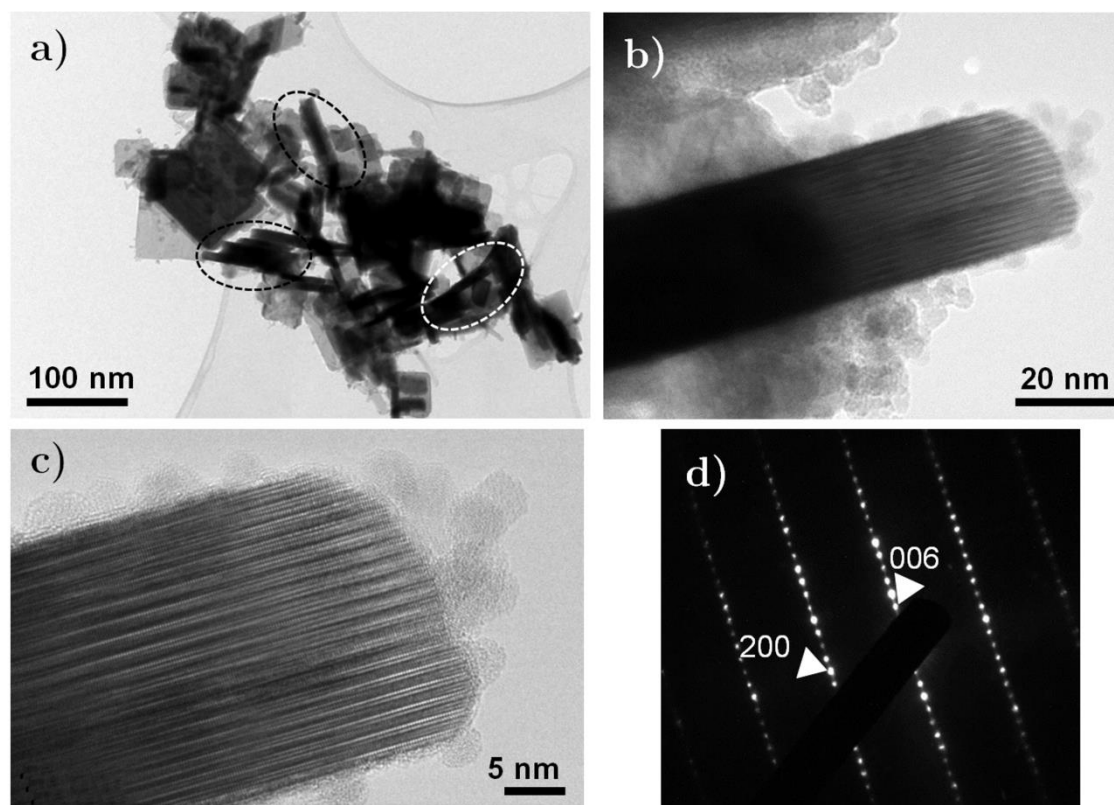


Figure 4.42: Representative TEM image a) and HREM image b) and c) with a corresponding SAED pattern d) of FBIT sample hydrothermally treated for 1 h at 180 °C in the presence of hydrazine. The SAED pattern was indexed according to the tetragonal structure of BIT along $[010]_{\text{BIT}}$.

Beside the BIT nanoplatelets covered with amorphous nanoparticles, the sample FBIT-180/1-HID also contained larger, octahedral particles (Figure 4.43 a)). The SAED pattern taken on the single nanoparticle from Figure 4.43 a) could be indexed according to the cubic spinel structure orientated along $[011]_s$. Moreover, TEM analysis reveals that also the size of particles of the other secondary phases present increased. Figure 4.43 b) shows 10 nm wide and over 200 nm long elongated particles of $\alpha\text{-FeOOH}$.

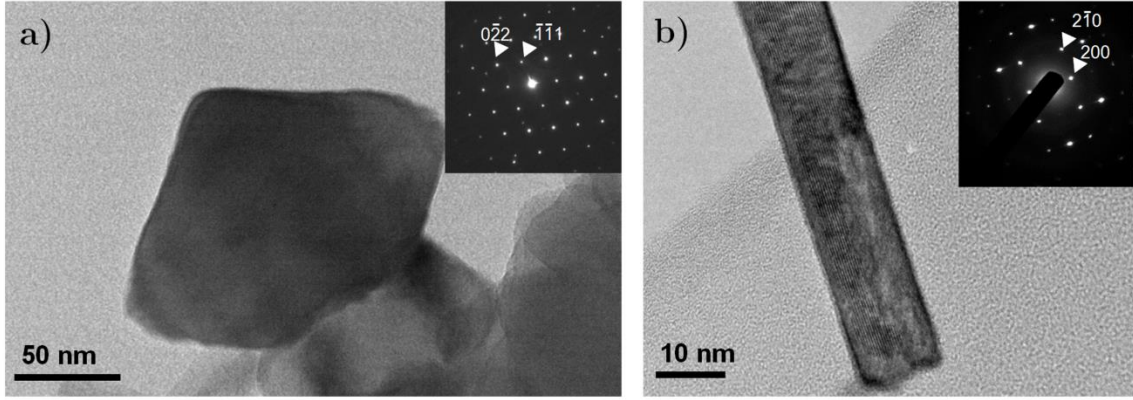


Figure 4.43: TEM image of separate particles of maghemite a) (inset: SAED pattern indexed according to spinel structure along $[011]_S$) and goethite particle b) (inset: SAED pattern indexed according to α -FeOOH structure along $[001]_G$) The FBIT sample was hydrothermally treated for 1 hour at 180 °C in the presence of hydrazine.

The magnetic properties of the FBIT samples, which were hydrothermally treated for 1 hour at different temperatures (under ambient and reductive conditions) are shown in Figure 4.44. The M_S of the samples hydrothermally treated without hydrazine does not significantly change compared to the sample FBIT. On the contrary, the magnetic measurements of the FBIT samples, which were hydrothermally treated under reductive conditions, showed an increase in the M_S compared to the FBIT sample. While the M_S of the sample treated at 160 °C increased just slightly, the significant increase in M_S was observed for the sample FBIT-180/1-HID. The increase of the M_S resulted from the presence of the larger, octahedral spinel-ferrite particles. However, the M_S of the sample is still significantly lower compared to the M_S expected if the whole iron would precipitate in the form of maghemite ($M_{S(est)} \approx 8 \text{ Am}^2/\text{kg}$).

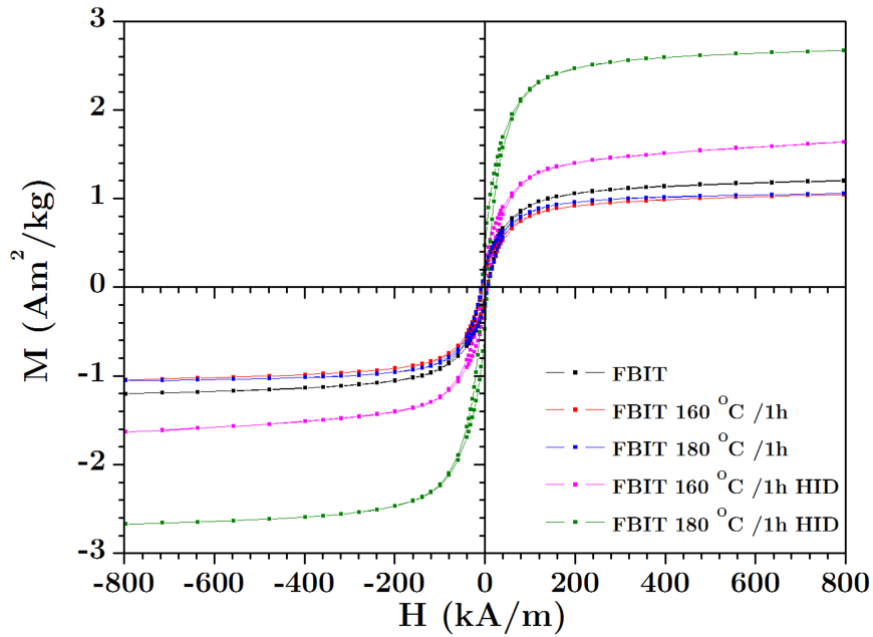


Figure 4.44: Magnetic hysteresis of the hydrothermally treated FBIT sample for 1 hour at different temperatures compared to the hysteresis of the initial FBIT.

I assumed that the Fe-rich, amorphous nanoparticles attached to the surfaces of the BIT nanoplatelets will crystallize during the hydrothermal treatment. However, the results showed that the nanoparticles remained amorphous even when the conditions were appropriate for the formation of the magnetic spinel iron oxide [22]. This could indicate that the BIT nanoplatelets influence the crystallization of the spinel-ferrite. They can influence the formation by partial dissolution and release of the species, which interfere with the formation of the spinel ferrite. During the hydrothermal treatment under reductive conditions at 180 °C separate maghemite particles were formed. Maghemite nanoparticles could be formed as a result of the reduction of the $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles [121].

4.2.2.2.2 Annealing of the FBIT sample

The effect of high temperature on the FBIT sample was also evaluated with annealing the sample for 2 hours at different temperatures (500 – 700 °C). I assumed that the amorphous nanoparticles would crystallize with the annealing. Moreover, at temperatures above 600 °C, the transformation of the maghemite into the non-magnetic hematite is expected [22].

The TEM analysis of the FBIT sample annealed for 1 hour at 500 °C revealed that the size of BIT cores significantly increased (Figure 4.45 a)). The small, approximately 5-10 nm large Fe-rich nanoparticles still remained at the BIT core nanoplatelets (Figure 4.45 b) and c)). HRTEM imaging showed that the nanoparticles at the surfaces of BIT nanoplatelets remained amorphous even after annealing at 600 °C.

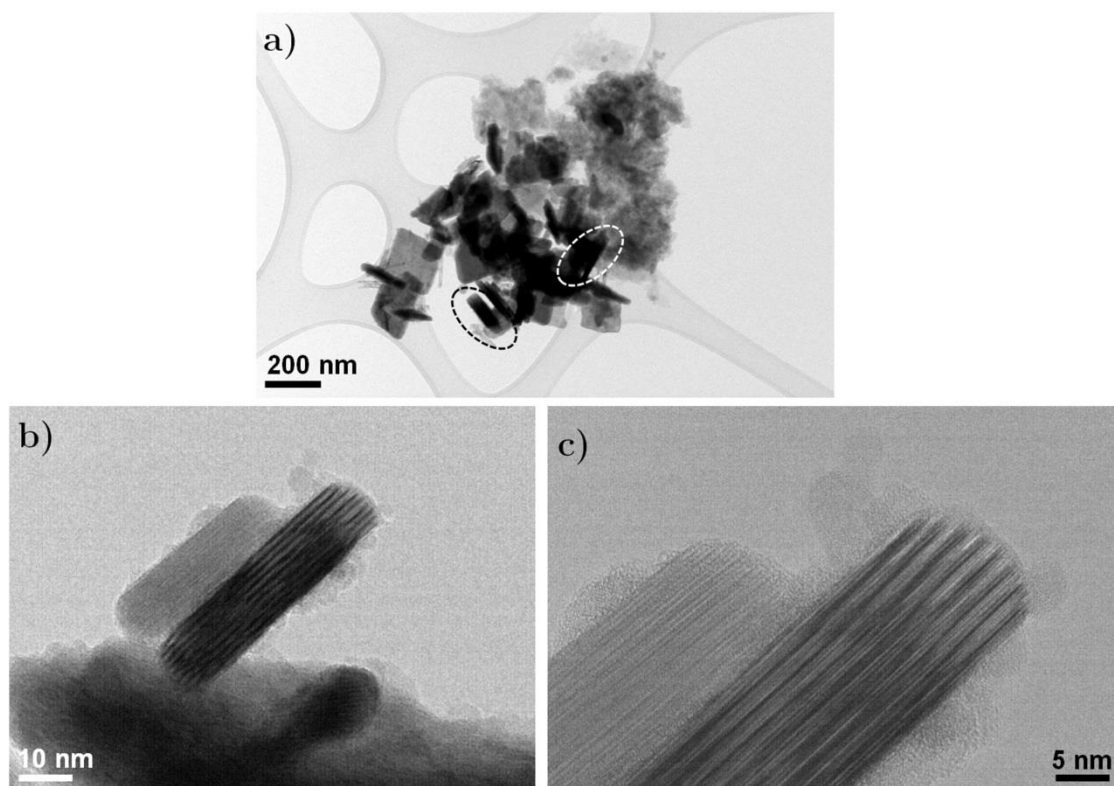


Figure 4.45: Representative TEM image a) and HRTEM images b) and c) of FBIT sample annealed for 2 h at 500 °C.

Figure 4.46 a) shows a representative TEM image of the FBIT sample annealed for 2 hours at 700 °C. TEM analysis showed that at this high temperature the nanoparticles grow and their shape became more isotropic. At 700 °C, the BIT reacted with the Fe-rich nanoparticles. The detailed observation of the sample (Figure 4.46 b) and c) showed that the BIT core nanoparticles are no longer covered with small nanoparticles, as it was observed after annealing at the lower temperatures. HRTEM showed that the nanoparticles frequently consist of the BIT core and the surface phase (Figure 4.46 c)). The EDXS showed the presence of Bi, Ti, and Fe across the whole particle; however the concentration of Fe was higher in the surface phase. The sample also contained well-crystalline isotropic particles (Figure 4.46 d)) containing all the three cations, confirming chemical reaction between the Fe_2O_3 and BIT.

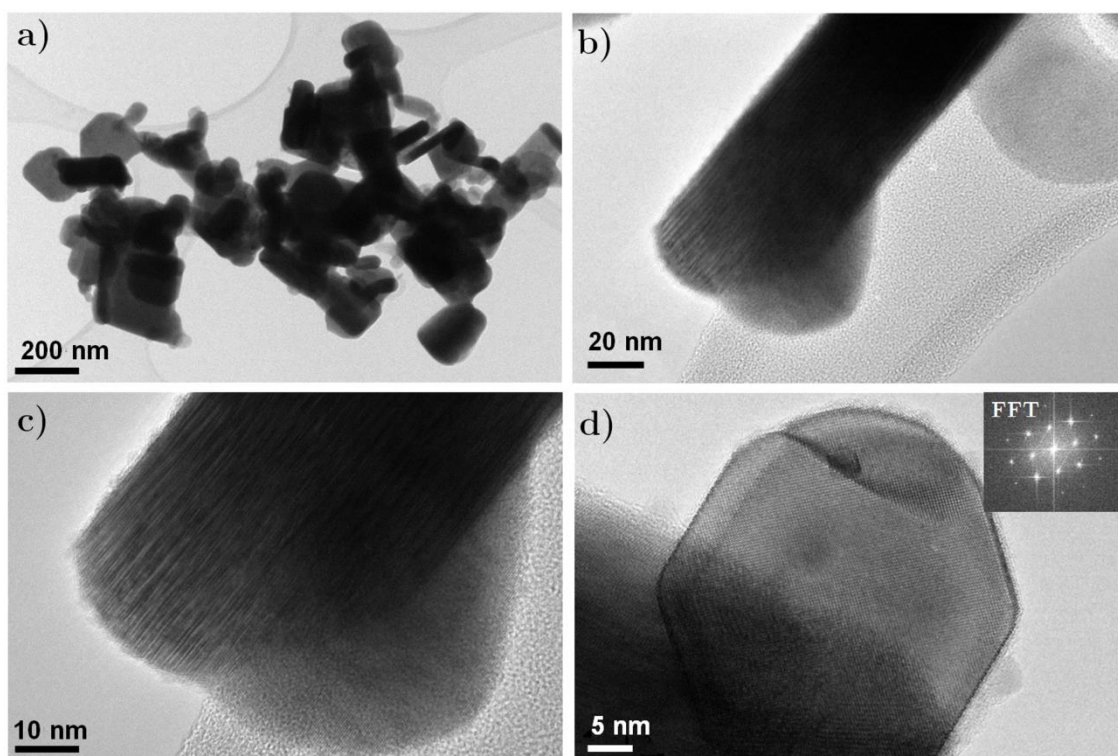


Figure 4.46: Representative TEM image a) and HRTEM images b) - d) of FBIT sample annealed for 2 h at 700 °C (inset of d) shows a corresponding FFT pattern).

Figure 4.47 shows magnetic properties of annealed FBIT samples. The measurements showed that the M_s of the FBIT sample annealed at 500 °C did not change when compared to the initial FBIT. The results are consistent with the TEM analysis showing no obvious changes in the crystallinity of the Fe-rich phase. With increasing the annealing temperature, the M_s of the samples decreased. The sample FBIT-600 °C displayed increased H_C compared to the FBIT sample, suggesting a small content of larger magnetic nanoparticles. With annealing of the sample at 700 °C the sample became paramagnetic. The decrease in M_s is obviously the result of chemical reactions of the Fe-rich phase with the BIT matrix.

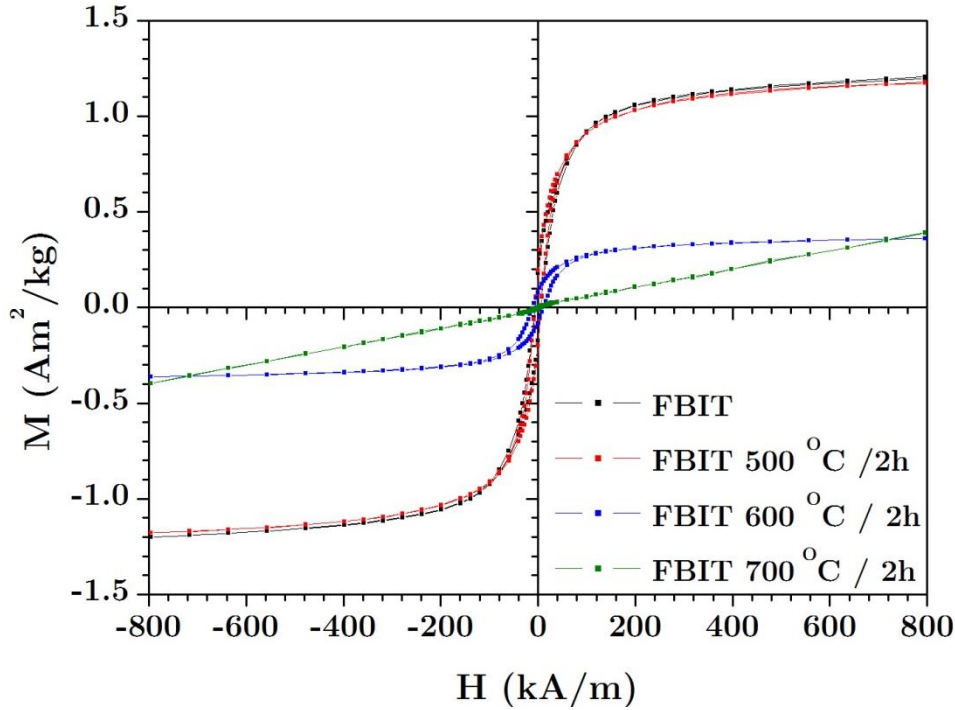


Figure 4.47: Magnetic properties of the FBIT samples annealed for 2 hours at different temperatures.

According to the applied experimental conditions it is expected that the amorphous nanoparticle will crystallize as the maghemite during the annealing at temperatures, before they will react with the BIT. On the contrary, the results showed that the Fe-rich nanoparticles attached to the surfaces of the BIT nanoplatelets remain amorphous even at temperatures up to 600 °C. The reason why the nanoparticles did not crystallize remains unclear.

4.2.2.2.3 Influence of the nanoplatelets surface on the formation of iron-oxide shell

As stated above, the controlled precipitation results in remarkably different products when BIT nanoplatelets and hexaferrite nanoplatelets are used as the cores. This can be related to two possible explanations. The first explanation can be related to structural dissimilarities between the BIT and the maghemite structures. In the case of the hexaferrite cores it was shown that the crystal structure of the core nanoparticles significantly influences the maghemite formation. The maghemite deposited exclusively onto basal surfaces of hexaferrite core nanoplatelets, where the two structures closely match, whereas it was never located at the side surfaces, where there is no matching between the two structures. Due to the structural similarities between the two structures the maghemite layer grows epitaxially on the basal surfaces, forming a low-energy, coherent interface [72]. However, the maghemite also deposited onto the amorphous silica core nanoparticles in the form of randomly orientated nanoparticles.

I assumed that the dissimilarities between the two crystal structures, the maghemite and the BIT, could influence the formation of the maghemite nanoparticles with heterogeneous nucleation. Generally, the heterogeneous nucleation is favored compared to the homogeneous nucleation because the solid-solid interfacial energy is smaller than the solid-solution energy. Therefore, the formation energy of nanoparticles is lower in the case of the heterogeneous nucleation. Energy needed for the heterogeneous nucleation is

especially low when the crystal structure of the core nanoparticles enables the formation of coherent, low-energy interface. In the case of the hexaferrite core nanoplatelets the structure is always terminated at the basal surfaces with a cubic “S” structural block, which is basically the (111) slice of the spinel structure. The outer-most S block of the hexaferrite structure simply extends with the deposited maghemite layers. On contrary to the hexaferrite, the BIAT structure is not structurally related to the spinel structure of the shell. The dissimilarities between the crystal structures of the maghemite and the BIT nanoplatelets increase the formation energy of the maghemite shell. Due to the increased formation energy, the iron-rich amorphous nanoparticles (probably iron oxide-hydroxide) could not crystalize under mild reaction conditions that were used in the controlled co-precipitation process [72, 76].

The second reason for the formation of the amorphous nanoparticles on the surface of the cores could be related to partial dissolution of the BIT nanoplatelets. The presence of foreign ions in the reaction mixture can change the formation process of the maghemite nanoparticles and determine the final phase on the surfaces of the BIT nanoplatelets.

To exclude the assumption that the structural dissimilarities between the two structures influence the maghemite formation the BIT nanoplatelets were coated with an approximately 10 nm thick silica layer. The BIT nanoplatelets were coated using the modified Stober process [88] (sample BIT-Si). Our previous research has shown that the maghemite formed at the surfaces of silica nanoparticles after the heterogeneous nucleation [76]. I expected that the maghemite would also be formed on the surfaces of BIT-Si nanoplatelets in the same way. The deposition of the spinel-ferrite onto the BIT-Si nanoplatelets proceeded as in the case of the sample FBIT.

TEM analysis of the FBIT-Si sample showed amorphous Fe-rich nanoparticles attached to the BIT-Si cores as in the case of the nanoplatelets without the silica coating (Figure 4.48 a) and b)).

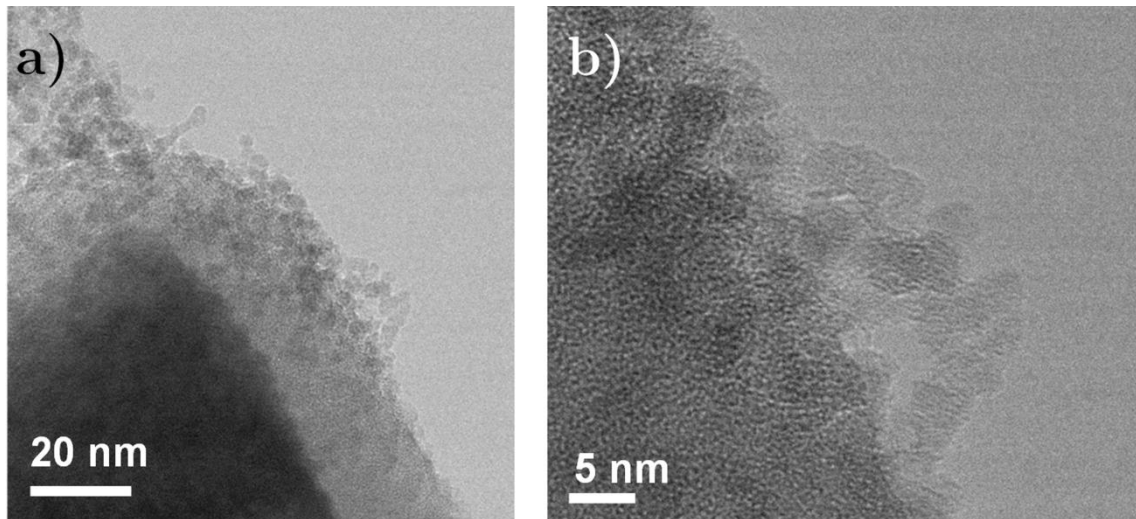


Figure 4.48: TEM images of amorphous Fe-rich nanoparticles deposited onto the silica-coated BIT particles of the FBIT-Si sample.

With coating the BIT nanoplatelets with the silica layer I wanted to exclude the influence of the structure of the core on the formation of the maghemite. However, the nanoparticles attached to the BIT-Si nanoplatelets remained amorphous suggesting that the structure of the BIT nanoplatelets is not critical for the formation of the maghemite.

Considering the results I assume that the formation of the maghemite nanoparticles on the surface of the cores is influenced by partial dissolution of the BIT nanoplatelets.

In my preliminary experiments I also tried to deposit the spinel-ferrite on the BIT nanoplatelets coated with a thinner, approximately 3 nm thick silica layer. It was observed that the silica layer was not present on the surfaces of the BIT nanoplatelets after the coating process. This can be the indication that the nanoplatelets were slowly dissolving and by their partial dissolution the silica layer decomposed. To point out the component of the reaction mixture, which is responsible for possible dissolution of the BIT cores, I exposed the silica-coated nanoplatelets to the aqueous solutions of the individual components of the reaction mixture at the room temperature and at 60 °C. When the silica-coated BIT nanoplatelets were exposed to the aqueous solutions of iron nitrates TEM analysis showed that the silica at the nanoplatelets remained intact. When the urea was added in the solution containing silica-coated BIT nanoplatelets the silica remained intact after the aging at room temperature. However, when the suspension containing the silica-coated BIT nanoplatelets and the urea was aged at 60 °C the TEM showed complete degradation of the silica layer already after 30 minutes. When the silica-coated hexaferrite nanoplatelets were exposed to the urea solution, the silica remained intact. The results indicate that the silica layer degraded from the BIT nanoplatelets, most probably because of the dissolution of the BIT nanoplatelets. It is known that the urea forms coordination compounds with various metal ions [122]. Therefore, the urea, which releases with the decomposition of the Fe-urea complex, could promote the dissolution of BIT nanoplatelets.

The silica layer does not completely isolate the BIT nanoplatelets from the surrounding, due to its porosity. I assume that even when the BIT cores were coated with a thicker more than 3 nm thick silica layer, the solute ions diffuse through the layer into the reaction mixture.

The presence of impurities in the solution could influence the formation of the maghemite nanoparticles. The change in the formation of maghemite nanoparticles could explain the formation of the amorphous nanoparticles on the surface of the BIT nanoplatelets.

4.2.2.3 Deposition of maghemite shell onto bismuth-titanate core nanoplatelets under reductive conditions

The results presented in Section 4.3.2.1 showed that the maghemite could not be formed on the surfaces of the BIT nanoplatelets using the same experimental conditions, as they were used for the deposition of the maghemite layers onto the hexaferrite cores. The reason is most probably related to the partial dissolution of the BIT cores in the presence of the urea. In the following experiments I therefore changed the experimental conditions that favor the spine-ferrite formation. As presented in Section 4.1.4, the formation of the spinel ferrite with controlled precipitation was favored at a lower temperature of 45 °C, when the pH of the starting reaction mixture was increased to be close to the pH required for the Fe^{2+} precipitation, and a reducing agent hydrazine was present. The reactions were conducted in the suspensions of the uncoated (BIT) and silica-coated (BIT-Si) bismuth-titanate nanoplatelets.

First, the Fe-urea/ Fe^{2+} and hydrazine were added into the argon bubbled suspension of the BIT core nanoplatelet at room temperature. The pH of the reaction mixture was adjusted with a diluted NaOH solution to pH of 5 and heated to 45 °C. The $\text{Mg}(\text{OH})_2$ was added into the mixture immediately when it reached the final temperature. After the reaction mixture remained at the final temperature and pH for 2 hours, the sample (FBIT-HID and FBIT-Si-HID) was collected. As it was demonstrated in Section 4.1.4,

well-crystalline spinel iron oxide formed under such conditions when the core nanoparticles were not present in the solution.

TEM analysis of the FBIT-HID sample where the iron oxide was deposited onto the uncoated FBIT core nanoplatelets revealed that the sample contained two types of the Fe-rich nanoparticles. Besides the BIT nanoplatelets agglomerates of smaller spherical, Fe-rich nanoparticles, 10-20 nm in size (Figure 4.49 a)) were present. SAED recorded on the agglomerate (Figure 4.49 b)) showed that the nanoparticles are well crystalline. The diffraction rings can be indexed according to the α -FeOOH and the spinel structures. Obviously, these Fe-rich nanoparticles were formed with homogeneous nucleation. The homogeneous nucleation is a consequence of a rapid increase in the pH after the addition of the hydroxide. The rapid release of the OH⁻ ions resulted in a high supersaturation of the precipitating product, which favors the homogeneous nucleation.

Detailed TEM analysis of the sample revealed that some of the BIT core nanoplatelets were covered with smaller approximately 5 – 10 nm large nanoparticles (Figure 4.49 c)). The HRTEM analysis revealed that the nanoparticles attached to the surfaces of the BIT nanoplatelets were amorphous (Figure 4.49 d)).

When the silica coated BIT nanoparticles were used as the cores (sample FBIT-Si-HID), the result was similar as in the case of the uncoated FBIT-HID sample. Also here, the nanoparticles attached to the surfaces of the silica-coated BIT nanoplatelets are amorphous.

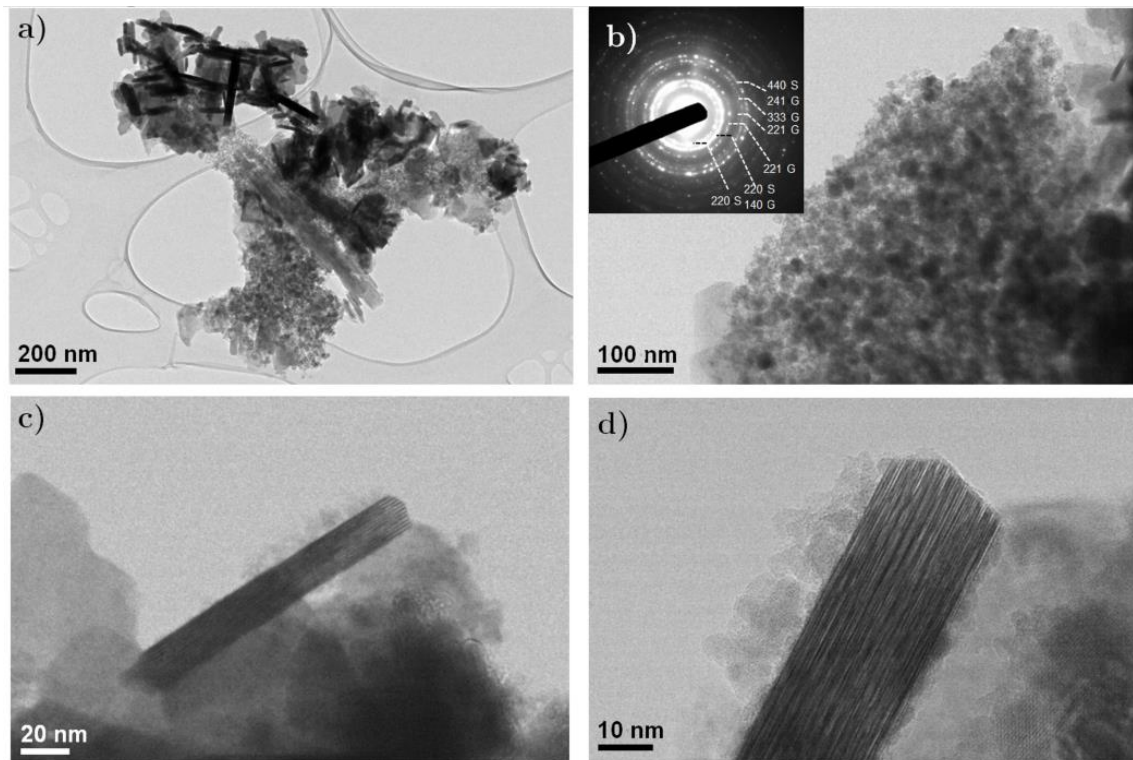


Figure 4.49: Representative TEM images of the FBIT sample: TEM image taken at low magnification a), TEM image of agglomerated Fe-rich nanoparticles with a corresponding SAED pattern b) (the pattern is indexed according to the spinel (S) and goethite structure (G)), and TEM images of BIT nanoplatelets with attached amorphous Fe-rich nanoparticles (c) and d)).

In Section 4.1.1.4.1 it was demonstrated that the spinel ferrite was formed under the reduction conditions at 45 °C (see the sample RTH5-45-0). The samples FBIT-HID and

FBIT-Si-HID were synthesized under equal reaction conditions as the RTH5-45-0 sample, except that the BIT nanoplatelets were present. Contrary to the situation without the core nanoplatelets, the Fe-rich nanoparticles were amorphous. Moreover, the samples contained besides a low amount of spinel-ferrite nanoparticles also a nonmagnetic secondary α -FeOOH phase, which was not observed in the RTH5-45-0 sample.

The results additionally support my conclusion that the formation of the spinel-ferrite nanoparticles is changed due to the partial dissolution of the BIT core nanoplatelets.

Chapter 5

General Discussion

Deposition of magnetic spinel-ferrite (magnetite and maghemite) shell on the surface of core nanoparticles is desired from the viewpoint of synthesis of new multifunctional materials. In particular, composite nanoparticles combining two magnetically different materials [12, 13, 21, 70, 72, 109, 123, 124] or combining magnetic material with materials of different functionalities, e.g., ferroelectric [115, 118], catalytic [125, 126], optical [127], plasmonic [128-131] materials, are especially interesting. The synergy between the different materials could result in improved or even completely new properties.

From different methods available for the synthesis of spinel ferrite nanoparticles only few can be used for deposition of the spinel-ferrite shell on the surfaces of core nanoparticles in the suspensions [11, 14, 62, 73, 132].

In my work, the spinel-ferrite shell was deposited on the surfaces of the core nanoparticles using the controlled co-precipitation method [76]. The method bases on the co-precipitation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions and heterogeneous nucleation of precipitating species on the surface of core nanoparticles. The method was already successfully used for the synthesis of bi-magnetic composite nanoplatelets combining maghemite layers deposited on the surface of the hexaferrite cores [72]. In my thesis I modified the method to allow control of the thickness of deposited maghemite layers on the surface of the hexaferrite cores. By varying the layer thickness the magnetic properties of the bi-magnetic composites could be tuned for the demands of specific applications [11-13, 17, 70]. For example, by combining soft-magnetic MnFe_2O_4 and hard-magnetic CoFe_2O_4 in the bi-magnetic composite the shape of the hysteresis loop was tuned in order to maximize the efficiency of conversion of electromagnetic energy into heat required for their use as mediators in magnetic hyperthermia cancer treatment [70].

In my work I successfully deposited differently-thick maghemite layers on the surface of hexaferrite core nanoplatelets. After the deposition, the bi-magnetic composite nanoplatelets retain a desired out-of-plane magnetization of the hexaferrite cores, while saturation magnetization M_s was successfully increased with the increasing thickness of the layer.

Furthermore, I tried to use the controlled co-precipitation method for coating the other functional materials with spinel-ferrite. In my thesis I tried to deposit the spinel-ferrite shell onto the surface of bismuth titanate (BIT) nanoplatelets. Bismuth titanate is a ferroelectric material. Combination of the magnetic shell and ferroelectric nanoplatelets can be beneficial for controlling the orientation of the ferroelectric nanoplatelets in the suspension with an applied magnetic field, or such composites can be used as building blocks for the preparation of magnetoelectric composites [117, 118, 133].

Using the same method that was used for successful deposition of the maghemite layers onto the hexaferrite cores, the spinel-ferrite shell could not be obtained on the surface of BIT core nanoplatelets. Moreover, the approximately 5 nm large Fe-rich nanoparticles that were attached on the surface of the BIT cores were amorphous. The sample contained also separate homogeneously nucleated nanoparticles of secondary phase α -FeOOH and α -Fe₂O₃. The result was much different than in the case of the bi-magnetic composites where maghemite was formed either in the form of epitaxial layers on the surface of the hexaferrite cores, or in the case of not optimal experimental conditions, in the form of separate, well crystalline particles.

To explain the reasons for differences between the deposition of the spinel-ferrite shell on the surfaces of the hexaferrite and on the BIT core nanoplatelets I systematically studied the chemical reactions involved in the controlled co-precipitation method. In the investigation I focused on the experimental conditions that could favour the crystallization of the precipitated products in the form of the magnetic spinel ferrite. The investigation showed that under the conditions that were used for the deposition of the maghemite layers on the surface of the hexaferrite cores, the sample does not contain only spinel-ferrite phase if the hexaferrite core nanoparticles were not present. Under the applied conditions some unwanted non-magnetic α -FeOOH and α -Fe₂O₃ secondary phases were formed. Since the experiment was conducted under the same reaction condition as in the case of the bi-magnetic composites, it is obvious that the core nanoparticles have an important role in the process of the spinel-ferrite formation with a controlled co-precipitation method.

In the case of the hexaferrite core nanoplatelets, the maghemite layers grow epitaxially at the basal surfaces of the core enabled by similarities between the two structures. Matching between the two structures decreases the energy of the interface between the hexaferrite core and the maghemite layer. Due to the decreased interfacial energy, the energy needed for heterogeneous nucleation of the layer on the basal surfaces of the hexaferrite cores is lower than needed for the heterogeneous nucleation at the side surfaces of the cores, and much lower to the energy needed for homogeneous nucleation of separate maghemite nanoparticles in the solution. Expected large differences between the energies for the different nucleation processes increase the sensitivity of the process to the experimental conditions applied during the deposition. For example, the uniform bi-magnetic composite nanoplatelets with differently thick maghemite layers were synthesized with a wide range of the iron-precursor concentrations (the Fe/HF molar ratio). If the epitaxial growth was prevented by coating the hexaferrite core nanoplatelets with a thin, amorphous silica layer, the composite was only obtained within a narrow range of concentrations. The maghemite deposited on the silica-coated nanoplatelets non-uniformly, in a form of small (≈ 5 nm), poorly crystalline nanoparticles (Figure 5.1.).

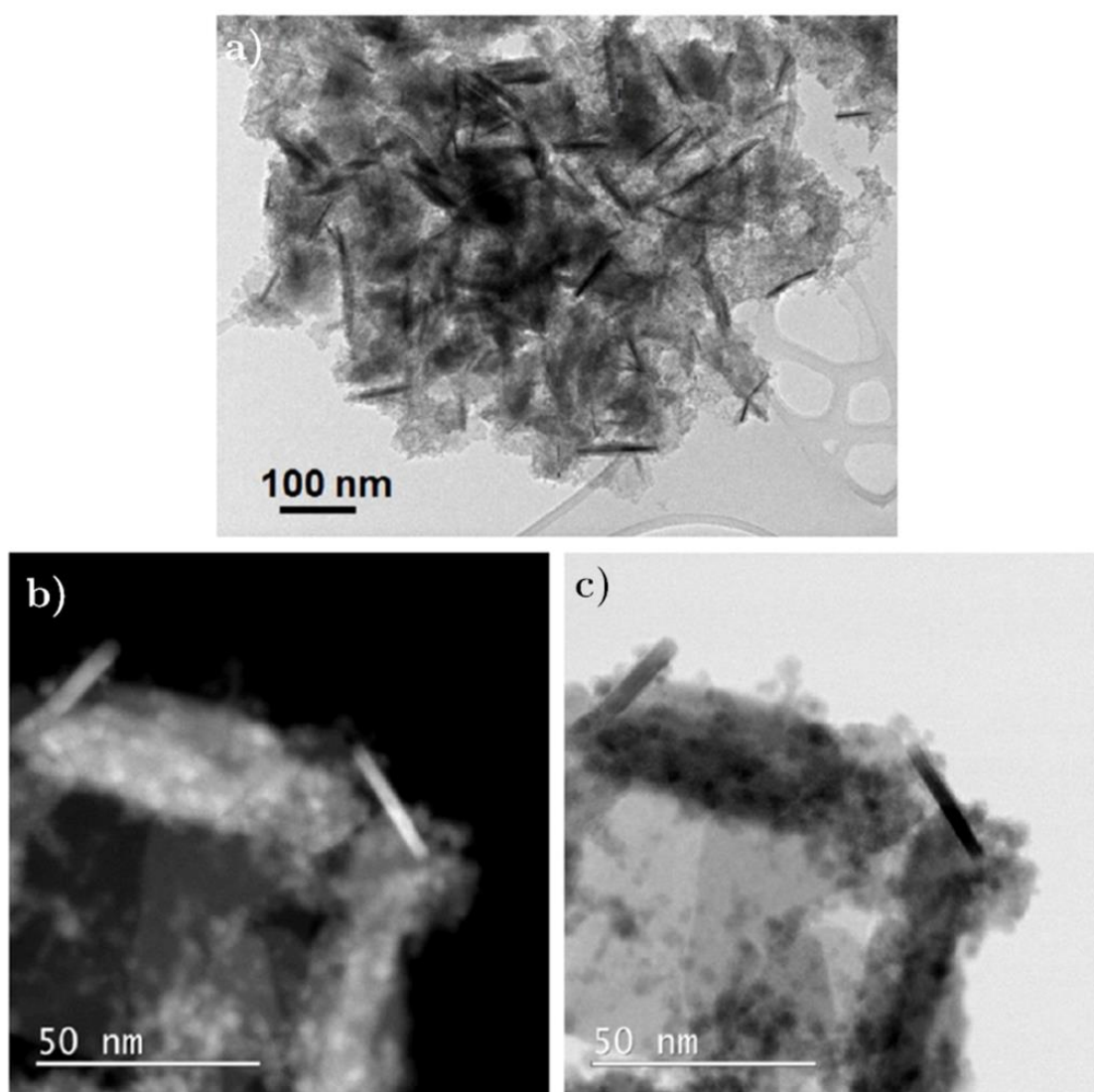


Figure 5.1: TEM a), HAADF STEM b) and BF STEM c) images of the maghemite deposited onto the silica-coated hexaferrite nanoplatelets.

Moreover, the particles with their structure matching the structure of the nucleating phase allow epitaxial growth of the nuclei at the lower supersaturation levels compared to the homogeneous nucleation in the solution [37]. Depending on the reaction conditions, different iron oxide hydroxide phases could be obtained with hydrolysis of hexaaqua ions ($[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$). At a low reactant concentration, the hexaaqua ions predominantly hydrolyze into γ -FeOOH, while at increased temperature and/or prolonged reaction, parallel formation of α -FeOOH can be observed. The formation of FeOOH is size dependent. The formation enthalpy for α -FeOOH (-561.5 kJ/mol) is lower than the enthalpy for γ -FeOOH (-552 kJ/mol), therefore the α -FeOOH is thermodynamically more stable. However, at a very small particle size, the hydration enthalpy becomes the important parameter, due to the increased surface-to-volume ratio. Hydration enthalpy for γ -FeOOH (0.40 J/m²) is lower compared to the α -FeOOH (0.6 J/m²), which increases thermodynamic stability of γ -FeOOH at a smaller particle size. Therefore the γ -FeOOH phase formed on the surface of the core nanoparticles could remain stable through a broader pH range compared to the one formed with homogeneous nucleation [92, 134].

The single-phase spinel-ferrite was not obtained when the core nanoparticles were not present, however, in the case of the BIT core nanoparticles the spinel-ferrite was not formed even when the sample was subsequently hydrothermally treated or annealed at high temperatures above 500 °C. The Fe-rich nanoparticles attached at the surface of the BIT cores were amorphous. Moreover, the attached nanoparticles remain amorphous even after annealing at 600 °C. This clearly shows that beside the structure of the core nanoparticles some additional factors influence the formation of the spinel-ferrite on the surface of BIT cores. For example, the spinel ferrite formation could be obstructed with ions, which appear as the consequence of a partial dissolution of the BIT core nanoplatelets. The assumption of partial dissolution was supported with the experiments where BIT nanoplatelets coated with thin (≈ 3 nm) silica layer were exposed to the aqueous solution of individual reactants. The experiment showed that the silica was degraded at 60 °C when the silica coated BIT nanoplatelets were exposed to the aqueous solution containing urea. I assumed that the silica degraded because of the partial dissolution of the BIT nanoplatelets. To additionally support the assumption, the supernatant was analysed for the presence of Bi and Ti. The analysis of the supernatant did not show any presence of Bi or Ti. Nevertheless, this could not disprove my assumption, as the concentration of the dissolved ions could be very low, under the detection limit, but they can still influence the spinel-ferrite formation. The assumption was also supported with experiments conducted under reducing conditions, which favour the formation of the spinel ferrite. When the core nanoparticles were not present, the single-phase spinel ferrite formed under the reductive conditions at 45 °C. On the contrary, when the BIT (silica-coated or uncoated) cores were present, the Fe-rich nanoparticles attached on the BIT remained amorphous.

The partial dissolution of the BIT cores could be promoted by urea, which is released in the reaction mixture with thermal decomposition of the Fe-urea complex. The released urea can form coordination compounds (complexes) with the ions from BIT. It is known that the urea can form a water soluble nitrate or chloride complexes with various metal ions such as Cu (II), Co (II), Mn (II), Fe (III), Mo (III), Mo (IV), and also Ti (IV) [122, 135]. The complexes can be formed at 60 °C, the temperature of spinel-ferrite deposition [122]. Urea coordinates the ions through oxygen or nitrogen atoms, which act as electron donors [136]. Therefore possible formation of such a complex with solute ions could influence the formation of the spinel-ferrite nanoparticles.

As it is known, certain reaction conditions in the co-precipitation process (e.g., type of counter ions, temperature, reactant concentrations, impurities, which could form coordination compounds with the constituting ions) have a large impact on the physical, chemical and structural properties of the nanoparticles [137-139]. For example, it was reported that the polypeptides containing acidic amino acids (aspartamic, glutamic acid) stabilize the precursor and they can influence the crystal size by delaying the nucleation and obstructing particle growth. The negatively charged proteins inhibit the formation of the spinel-ferrite as they likely inhibit the nucleation by the stabilization of amorphous nanoparticles through the coordination of iron [140]. Pušnik et al. [138] showed that the presence of aspartic acid shifts the precipitation of the iron ions to a higher pH compared to the co-precipitation of the iron ions alone due to the formation of a coordination compound with the Fe^{3+} ions. The reaction is much slower and depending on the reaction conditions can lead to the formation of non-magnetic secondary $\alpha\text{-Fe}_2\text{O}_3$ phases. However, those compounds, which influenced the formation of the spinel-ferrite, were present in the reaction mixture in much higher concentration than in our case, where the detection of possible solute ions was not possible with simple analytical methods.

However, it could be possible that amorphous nanoparticles attached on the surface of the BIT core nanoplatelets could result from the formation of the urea complex with the ions dissolved from BIT (Ti or Bi). The complex could inhibit the formation of the spinel-ferrite by reacting with precipitating species and stabilizing the amorphous nanoparticles.

In my thesis I showed that the controlled co-precipitation method could not be used for deposition of the magnetic spinel-ferrite layers on any core nanoparticles. The controlled co-precipitation can, however, be very successfully used for the deposition of the maghemite layers onto the surfaces of the hexaferrite core nanoplatelets. With varying the thickness of the maghemite layers on the basal surfaces of the hexaferrite cores I synthesized the bi-magnetic nanoplatelets displaying extraordinary magnetic properties: rigid exchange coupling, out-of-plane easy axis of the magnetization, and strongly improved M_s . The M_s varied from 36 Am²/kg for composites with the thinness, 1.1 nm thick maghemite layers, to 50 Am²/kg for the composites with the thickest, 2.5 nm thick layers. Those properties are believed to be very important for the development of completely new magneto-responsive materials and applications based on aligning the nanoplatelets with an applied magnetic field.

The controlled co-precipitation method enables incredible control over the deposition of the maghemite layers onto the hexaferrite nanoplatelets resulting in the uniform structure of the bi-magnetic nanoplatelets. Such incredible control of the layer deposition process is usually associated with expensive high-vacuum methods, such as molecular-beam epitaxy [141-143]. The uniform bi-magnetic composite nanoplatelets with a different thickness of the maghemite layers were synthesized in a wide range of the iron-precursor concentration. This robustness of the deposition process can enable the scale-up of the controlled co-precipitation process for a mass production. Our controlled-precipitation method is an alternative to methods, which are based on the deposition of the spinel-ferrite shells at the core nanoparticles with a thermal decomposition of organometallic compounds in high-boiling point solvents [12, 13, 65, 70, 124]. The thermal-decomposition method also enables close control of the deposition process. However, the disadvantages of the method are in its high complexity due to use of toxic, expensive starting materials, which all makes scaling up the synthesis very difficult.

Compared to the thermal decomposition method, the controlled co-precipitation method enables the use of inexpensive starting materials, deposition of the layers at relatively low temperatures, in aqueous medium. This makes the process environmentally friendly, inexpensive, and appropriate for scaling up.

Chapter 6

Conclusions

The thesis was aimed to synthesise multifunctional composite nanoparticles with the deposition of magnetic spinel-ferrite shells onto surfaces of different core nanoparticles. The shell was deposited using a controlled co-precipitation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions and a heterogeneous nucleation of the precipitating products on the surfaces of the core nanoparticles in the aqueous suspension.

First, the controlled co-precipitation method was modified to enable deposition of the maghemite layers of controlled thickness onto surfaces of hexaferrite core nanoplatelets. The bi-magnetic maghemite-hexaferrite-maghemite sandwich nanoplatelets with improved magnetic properties were synthesized. The composite nanoplatelets showed an incredibly uniform structure defined by uniform structure of the hexaferrite cores and the homogeneous thickness of the maghemite layers, which epitaxially grew exclusively at the basal surfaces of the cores. The layer thickness was controlled by varying the ratio between the iron precursors and the hexaferrite cores, or by deposition of the layers in two subsequent steps. The bi-magnetic composite nanoplatelets displayed a single-phase hysteresis loop indicating that the two magnetically-different phases are rigidly exchange coupled. They retained the out-of-plane easy axis of the hexaferrite core nanoplatelets, while the saturation magnetization M_s was significantly improved. The M_s increased proportionally with the layer thickness. However, with the increase in M_s the coercivity H_C significantly decreased. The decrease in H_C was related to changes of the magnetic properties caused by a structural stress in the hexaferrite cores induced by the epitaxial maghemite layers.

In the second part of my thesis I tried to use the controlled co-precipitation method for deposition of the maghemite shell onto the surfaces of the bismuth titanate core nanoplatelets. Contrary to my hypothesis it appeared that the method could not be used for deposition of the magnetic shell onto any core nanoparticles. It appeared that under the same experimental conditions as used for successful deposition onto the hexaferrite cores, the maghemite could not be deposited on the bismuth titanate (nanoplatelets). The Fe-rich nanoparticles attached to the surfaces of the BIT cores remained amorphous and some non-magnetic secondary phases formed. The striking influence of the core nanoparticles on the co-precipitation was ascribed to (i) crystalline structure of the core, which enables the formation of low-energy, coherent interface with the maghemite shell in the case of the hexaferrite core, and (ii) to partial dissolution of the BIT core nanoplatelets in the reaction mixture influencing the chemical reaction of co-precipitation. Moreover, the single-phase maghemite could not be prepared neither when the experiment proceed under the same reaction conditions as were used for deposition of maghemite layer onto the hexaferrite cores, however, without the core nanoparticles. This

indicates that the core nanoparticles significantly influence the formation process of spinel-ferrite with controlled co-precipitation method.

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Original Scientific article

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Biography

I was born on 13 December 1989 in Maribor. After finishing the Bishop Gymnasium Anton Martin Slomšek Maribor in 2008 I decided to enroll to the Faculty of Chemistry and Chemical Technology (study program Chemical/Biochemical Technology) at the University of Maribor. In 2009, I started receiving a scholarship from the Jožef Stefan Institute and as a student I was doing occasional work as a tutor for the younger students at the faculty. I was also involved in laboratory work at the Institute of Public Health and Department of Genetic and Genomic at the Faculty. In 2012, I received the Dean Award for the research work in the field of genetics entitled: Analysis of candidate genes occurring in inflammatory bowel disease in correlation to the biological drug adalimumab. In 2012, I started my internship and diploma research at the Jožef Stefan Institute in the Department for Material Synthesis. I graduated in September 2013 with a diploma thesis entitled: *Synthesis of composite nanoparticles using coating of the core nanoparticles with spinel ferrite layers*, under the supervision of Prof. Dr. Darko Makovec. In October 2013, I started working as a young researcher at the Jožef Stefan Institute in the Department of Material Synthesis. At the same time I enrolled the Nanosciences and Nanotechnologies postgraduate program at the Jožef Stefan International Postgraduate School. My work at the department was mainly related to the deposition of different thick maghemite layers on the surface of the hexaferrite core nanoparticles in order to engineer the properties of bi-magnetic nanoparticles. One part of the research was also to deposit the spinel-ferrite shell on the other core nanoparticles with different functionalities. My research work was awarded as Best Nano Paper in 2015 and 2016 at the Jožef Stefan Postgraduate Student Conference.